Characterization of Alumina and Removal of Sulphate Ions in Aqueous Stream Using Alumina Prepared by Precipitation Method

by

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Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

_____

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UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

July 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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SITI NOREHAN BINTI JAAFAR

ABSTRACT

Several studies have been done on discovering the potential of alumina as an adsorbent to remove heavy metal such as cadmium and anionic entities such as fluoride and phosphates. The main objective of this research is to produce aluminium oxide (Al_2O_3) via Precipitation method using only aluminium salt ($AlCl_3$) and ammonium hydroxide (NH_4OH) as starting materials. White gel precipitate was formed from this reaction. The precipitate was filtered, calcined, ground and sieved to get alumina particles with desired particles size and adsorbent characteristics. The calcinations temperature was chose to be 750^oC and the particles size of the alumina was in a range of 500-1000 micrometer. The alumina produced was characterized to know its organic structure, surface area and surface morphology. The adsorption capacity towards metal ion was determined using DR/4000 Spectrophotometer by applying Method 8051.

The synthesized adsorbent has BET surface area of 166 m^2/g and average pore diameter of 8.6 nm. Percent metal uptakes of sulphate ion were increased with increasing concentration of initial sulphate concentrations. The adsorption was optimized at the initial concentration of 50 ppm for synthesized alumina and 40 ppm for commercialized alumina. Adsorption of sulphate ion onto surface of alumina has occurred proportionally with increasing contact time while equilibrium point was attained after 45 minutes for synthesized alumina and 55 minutes for commercialized alumina. The data of adsorption studies on synthesized alumina was found to be fitted the Langmuir and Freundlich isotherm with linear regression constant of 0.99 and 0.98 respectively while commercialized alumina can be represented by Langmuir model.Kinetic study shows that the adsorption using synthesized and commercialized alumina follows pseudo second order kinetics with correlation coefficient of 0.96 and 0.98 respectively which relies on the assumption that chemisorptions may be the rate limiting step.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS AND NOMENCLATURE

WHO	World Health Organization
TOC	Total Organic Carbon
BOD	biochemical oxygen demand
COD	Chemical Oxygen Demand
TOD	Total Oxygen Demand
FTIR	Fourier Transform Infra Red
FESEM	Scanning Electron Microscopy
BET	Brunauer, Emmett and Teller
UV	Ultraviolet
TGA	Thermogravimetric Analysis
XRD	X-ray Diffraction
ϒ	Gamma
M	Mole
Rpm	Revolution per Minute
Ppm	Part per Million
γ-AlO (OH))	Boehmite
IR	Infrared
Al_2O_3	aluminium oxide
HCl	hydrochloric acid
$AlCl_3.6H_2O$	aluminium hexahydrate
NH_4OH	ammonium hydroxide
BaSO4	barite
MgSO4·7H2O	epsomite

CHAPTER 1

1.0 INTRODUCTION

1.1 Background Study

High concentration of sulphate in aqueous stream will give significant effect to human health and ecosystem. Sulphate is present in aqueous streams primarily from drinking water and wastewater stream such as from animal husbandry, mining, food processing, the pharmaceutical industry, pulp and paper wastewater, etc (Feng Zhao and co-workers, 2008).Concentration of 500mg/L is the maximum level of sulphate in drinking water as suggested by World Health Organization (WHO).The consumption of drinking water containing sulphate concentrations in excess of 600 mg/l commonly results in laxative effects .Regulatory agencies are becoming increasingly concerned over elevated sulphate concentrations in effluents, owing largely to its impact on the salinity of receiving waters. Presence of sulphate in wastewater caused changes in pH of water and affect solubility of metals and other substances. At very high concentrations, sulphate is toxic to cattle.

For these reasons, much effort and expenses has been undertaken to treat sulphate-rich stream. There are several methods for treating stream containing sulphate anions. The removal of this anion in wastewater stream by means of adsorption using activated carbon, neutralization with calcium carbonate, biological treatment, reverse osmosis, dialysis and ion exchange had been studied. The selection of the treatment method is usually based on the type of wastewater, removal rate, the waste concentration and cost of the treatment (Haghsheno and colleagues, 2009).

Biological sulphate reduction has been recognized as an efficient method. However, the main problem related to this process is due to generation of sulfide that inhibits bacterial growth, decreases the rate of sulphate reduction, and causes physical or biological constraints that may lead to process failure (Feng Zhao and colleagues, 2008).

Increasing concern over pollution causes by sulphate arising from different industrial activities require consideration of new alternatives. There are currently not many available papers which review on the use of adsorption in removal of sulphate from aqueous stream. Several adsorbents been used for removal of sulphate ions from aqueous stream are iron surface and sugarcane bagasses. However, current adsorption methods have several drawbacks such as lower ions selectivity and caused environmental problems (Feng Zhao and co-workers, 2008; Boukhalfa, C., 2010; Daniella and Maria, 2007).

Therefore, in this research the potential of aluminium oxide (Al_2O_3) prepared by precipitation method has been investigated. From the literature review, an established technique that is widely used to produce aluminium oxide (Al_2O_3) is extraction process. In extraction process, aluminium ore will be treated to extract pure aluminium oxide (Al_2O_3). However, this technique requires the digestion of aluminium ore with hydrochloric acid (HCl) for crystallizing of aluminium hexahydrate ($AlCl_3.6H_2O$).There are many problems associated with the use of hydrochloric acid in this process. High-energy expenses are required to drive off this gas. The absorption will be very unfavorable with the presence of highly concentrated hydrochloric acid solution and this process requires high consumption of cooling water (Belsky and colleagues, 1980).

High porosity aluminium oxide (Al_2O_3) can also be synthesized using sol-gel process using aluminium alkoxides as a precursor.This process is well-established because different marphologies,surface area and pore volumes of alumina is being formed in different processing conditions (S.Kureti,2001).However,this process requires use of chelating agent to control the hydrolisis rate due to the relatively high reactivity of aluminium alkoxides. High cost of this chelating agent is a major drawback in the commercialization of high-purity alumina (Ji-Young Park and co-workers, 2002).

Most of the commercialized aluminium oxide (Al_2O_3) is obtained by the calcinations of aluminium hydroxide using Bayer process which involves the digestion of bauxite in caustic soda and the subsequent addition of fine seed crystal of aluminium hydroxide. (Anonymous, 2010).Aluminium oxide (Al_2O_3) produced by this process

exists in many form such as alpha, beta, and gamma with alpha being the most thermodynamically stable .The variation in forms arises during the heat treatment of aluminium hydroxide or aluminium oxy hydroxide.

In this study, inexpensive inorganic salt raw materials have been used to replace aluminium alkoxide as aluminium precursor .Simple precipitation method will be used to produce aluminium hydroxide. Ammonium hydroxide will be mixed together with salts specifically aluminium chloride in aqueous solution. The aluminium hydroxide that forms from the reaction will then being converted into alumina through calcinations at temperature of 700^{o}C for 2 h. From literature review, this process was successfully been proven in synthesizing porous alumina with high surface area and a narrow pore size distribution (Ji-Young Park and co-workers, 2002).

The present study is initiated to evaluate the effectiveness of aluminium oxide (Al_2O_3) prepared by precipitation method as an adsorbent in the adsorption process for the removal of sulphate from aqueous stream. The adsorbent characteristics of aluminium oxide (Al_2O_3) prepared by precipitation will be compared to commercialized aluminium oxide (Al_2O_3). Laboratory batch adsorption and adsorption kinetics studies are conducted to determine the adsorption capacity of aluminium oxide (Al_2O_3). The parameters that may affect the adsorption process are the initial concentration of adsorbate, pH of solution and the amount of adsorbent. The equilibrium time is evaluated based on the contact time. The adsorption kinetic will also be studied to know the time dependence of adsorption on solid surfaces.

1.2 Problem Statement

1.2.1 Problem Identification

According to Metcalf and Eddy (2003), sulphate is categorized as dissolved inorganic constituent. Sulphate is added to the original domestic water supply as a result of water use and has to be removed if the wastewater is to be reused. The typical concentration ranges of 20mg/L, 30mg/L and 50 mg/L for sulphate in

untreated domestic waste-water are considered weak, medium and high respectively. For humans, concentrations of 500 - 750 mg/L cause a temporary laxative effect. At very high concentrations sulphate are toxic to cattle. Problems caused by sulphate are most often related to their ability to form strong acids which changes in the pH. Sulphate ions also are involved in complexing and precipitation reactions which affect solubility of metals and other substances.

Sulphate compounds are primarily used in the chemical industry. They become contaminant in industrial wastes and also pollutant through atmospheric deposition. However, groundwater and natural sources of sulphate contributes to the highest level of pollutant.In general, the average daily intake of sulphate from drinking-water, air and food is approximately 500mg, food being the major source. However, in areas with drinking-water supplies containing high levels of sulphate, drinking-water may become the major source of intake (WHO Guidelines for Drinking-water Quality, 2004).

Currently, no health-based guideline is proposed for sulphate. However, it is recommended that the authorities be notified if sulphate concentrations in drinking water exceed concentration of 500 mg/L. The presence of sulphate in drinking-water may also cause noticeable taste and may contribute to the corrosion of distribution systems.

1.2.2 Significance of Study

There are many ways to produce aluminium oxide (Al_2O_3) with higher porosity, narrower size distribution and larger surface area than the commercial aluminium oxide (Al_2O_3). However, most of the method is expensive and require complex procedures (Zainab and Rozaina,2008;Y.S Lin and G.Buelna,2001).Therefore, the potential of aluminium oxide (Al_2O_3) prepared by precipitation method using ammonium hydroxide as precipitating agent is being studied.The process is believed to be simple yet able to produce significant result. Moreover, the starting materials which are aluminium chloride and ammonium hydroxide are readily available at low

cost. The desired characteristics of alumina to be utilized as an adsorbent usually have mesoporous structure with effective surface area from 200m^2/g to 300m^2/g (Duong D. Do, 1998).

The adsorbent then will be subsequently used in adsorption studies. Several approaches has been tried to remove sulphate from aqueous stream (Balmat, 1980; Hendrix and colleagues, 1994; Barnes and Lionel John, 1990). However, these approaches usually treated sulphate when it has already formed a compound with other ions. It is better to treat the sulphate ions before it form compounds with other elements because the compound formed must be relegated to be use as a landfill and also has no economic values.

Adsorption is one of the viable approaches to achieve this requirement because compared with other removal process; this method is significantly economical and easier. One of the adsorption methods that have been tried is the adsorption of sulphate ions from aqueous solutions by iron surfaces. Ionic adsorption on metals has been detected indirectly by the effect on the electro capillary curve (Boukhalfa, 2010). However, this technique does not give complete sulphate removal because sulphate has to compete with other ionic substances available during adsorption process. In the experiment, sulphate ion does chemisorbed on iron coupons prepared, but it is more likely that it sorbs on oxide. It has to compete with other anions, specifically, chromate, hydroxyl and chloride to be adsorbed therefore decreasing the adsorption capacity.

1.3 Objectives and Scope of Studies

In order to complete this project within the time limit and the scope given, several objectives have been identified.

i. To synthesize aluminium oxide (Al_2O_3) using Precipitation Method.

ii. To characterize the aluminium oxide (Al_2O_3) and compare the result obtained with commercialized aluminium oxide (Al_2O_3).

iii. To study the adsorption kinetics and adsorption equilibrium of the aluminium oxide (Al_2O_3) as an adsorbent in sulphate adsorption from aqueous stream.

iv. To study the effect of initial sulphate concentration and pH on adsorption of sulphate.

CHAPTER 2

2.0 LITERATURE REVIEWS

2.1 Presence of sulphate in aqueous stream

2.1.1 Sulphate contamination in drinking water supplies.

The World Health Organization (WHO) suggest a limiting value of 250mg/L for sulphate present in drinking water. Because of the possibility of adverse physiological effects at higher concentrations, health authorities should be notified if drinking water sulphate concentrations exceed 500 mg/L.Sulfates occur naturally in numerous minerals, including barite ($BaSO_4$), epsomite($MgSO_4 \cdot 7H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) .These dissolved minerals contribute to the mineral content of many drinking-waters.Reported taste threshold concentrations in drinking-water are 250–500 mg/litre (median 350 mg/litre) for sodium sulfate, 250–1000 mg/litre (median 525 mg/litre) for calcium sulfate and 400–600 mg/litre (median 525 mg/litre) for magnesium sulfate (World Health Organization,2004).

Sulphate is a dissolved inorganic constituent that is added to the original domestic water supply as a result of water use and may have to be removed if wastewater is to be reused (Metcalf and Eddy Inc, 1991).The presence of sulphate in drinking-water can cause noticeable taste, and very high levels might cause a laxative effect in unaccustomed consumers. There are various contributors of sulphate formation such as fertilizer,chemicals,dye,glass and soaps production.They are also used in mining,wood pulp,metal and plating industries.Copper sulfate has been used for the control of algae in raw and public water supplies. Sodium, potassium and magnesium sulfates are all highly soluble in water, whereas calcium and barium sulfates and many heavy metal sulfates are less soluble.This unsoluble sulphate may form scale in a pipeline.The formation will indirectly effect the quality of drinking water supply.Atmospheric sulfur dioxide, formed by the combustion of fossil fuels and in metallurgical roasting processes, may contribute to the sulphate content of surface waters.

2.1.2 Waste Water Treatment and sulphate contamination

Chemical parameters associated with the organic content of waste-water include biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), and total oxygen demand (TOD). Inorganic chemical parameters include salinity, hardness, pH, acidity and alkalinity, as well as concentrations of ionized metals such as iron and manganese, and anionic entities such as chlorides, sulphates, sulfides, nitrates and phosphates. Table 2.1 shows typical concentration ranges for various constituents in untreated domestic waste-water. Waste-water is classified as strong, medium or weak, depending on its contaminant concentration.

Table 2.1: Typical composition of untreated wastewater

Contaminants	**Unit**	**Concentration**		
		Weak	**Medium**	**Strong**
Total solid (TS)	mg/L	350	720	1200
Settleable solids	mg/L	5	10	20
BOD_5 ,20^oC	mg/L	110	220	400
TOC	mg/L	80	160	290
COD	mg/L	250	500	1000
Nitrogen (total as N)	mg/L	20	40	85
Phosphorus	mg/L	4	8	15
Chlorides	mg/L	30	50	100
Sulphate	mg/L	20	30	50
Alkalinity (as $CaCO_3$)	mg/L	50	100	200
Grease	mg/L	50	100	150
Total coliforms	No/100 ml	10^6-10^7	10^7-10^8	10^7-10^9
Volatile organic compounds	µg/L	<100	100-400	>400

Source: Adapted from Metcalf and Eddy Inc., *Wastewater Engineering*, 3rd edition.

2.2 Adsorption Process

An array of suitable methods exists for the removal of sulphate from wastewater. These methods include microbiological reduction, neutralization of sulphate with lime and addition of organic solvent (Balmat, 1980; Hendrix and colleagues, 1994; Barnes and Lionel John, 1990). These methods usually are combined with mechanical process such as filtration, centrifugation and sedimentation to effectively remove the unwanted product. However, these methods have several disadvantages, which include incomplete sulphate removal, generation of waste products (e.g. Calcium Sulphate) that require disposal and further treatment and most of the methods require specific conditions that are hardly being achieved.

The use of solids for removing substances from either gaseous or liquid solutions has been widely used. This process, known as adsorption, involves the binding of molecules or particles from the gaseous or liquid phase onto the surface of a solid substrate *(*Ruthven, 1984). From the early days of using bone char for decolorization of sugar solutions and other foods, to the later implementation of activated carbon for removing nerve gases from the battlefield, to today's thousands of applications, the adsorption phenomenon has become a useful tool for purification and separation.

Adsorption phenomena is operative in most natural physical, biological, and chemical systems, and adsorption operations employing solids such as activated carbon and synthetic resins (Valenzuela and Myers, 1989) are used widely in industrial applications and for purification of waters and wastewaters. The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. As illustrated in Figure 2.1, the adsorbing phase is the adsorbent and the material concentrated or adsorbed at the surface of that phase is the adsorbate (Metcalf and Eddy, 2003).

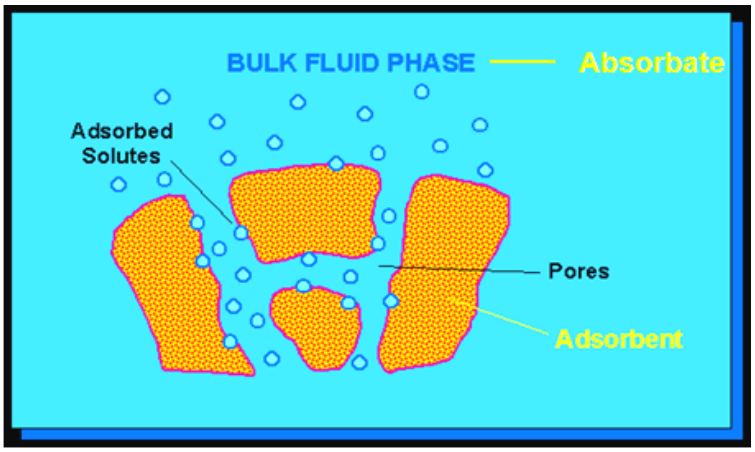

Figure 2.1: Illustration of adsorption process

Source: Adapted from Metcalf and Eddy Inc., *Wastewater Engineering*, 3rd edition

There are two principal modes of adsorption of molecules on surfaces which are physical adsorption and chemical adsorption. The basis of distinction is the nature of the bonding between the molecule and the surface. In physical adsorption, the only bonding is by the weak Van der Waals force. There is no significant redistribution of electron density in either the molecular or at the substrate surface. In chemical adsorption, the molecule is chemically bonded and substantial rearrangement of electron density is formed between the adsorbate and substrate (Tushar, 2004).

2.2.1 Adsorption Equilibrium

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The isotherm study is useful in describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate sorbent, and for preliminary determination of sorbent dosage requirements. Moreover, the isotherm plays an important role in the predictive modeling procedures for analysis and design of sorption systems. The Langmuir and Freundlich isotherms are most frequently used to represent the data of sorption from solution. In order to establish the maximum sorption capacity, the Langmuir equation as shown in Equation 2.1 was applied to the sorption equilibria at different adsorbent doses.

$$\frac{1}{q} = \frac{1}{Q\max} + \frac{1}{Ce} Q\max b \qquad \text{(Eq. 2.1)}$$

Where C_e is the concentration of the adsorbate solution at equilibrium (mg/l), q the amount of adsorbate sorbed at equilibrium (mg/g), Q_{max} the maximum sorption capacity of the adsorption system and b is constant related to the binding energy of the sorption system.

Linearised form of Freundlich equation was applied to the sorption equilibria at different adsorbent doses as shown in Equation 2.2.

$$\log q = \frac{1}{n} \log Ce + \log K \qquad \text{(Eq. 2.2)}$$

Where, K and 1/n are constants, which are considered to be the relative indicators of adsorption capacity and adsorption intensity (Unninathan and Anirudhan, 2007).

2.3 Adsorbent-Characterizations and Analytical Studies

According to 'Adsorbent Selection' report produced by Kent S.Knaebel, the most important attributes of adsorbent to be used in industrial process are capacity, selectivity, regenerability, kinetics, compatibility and also cost. Adsorption capacity also called loading is the most important characteristic of an adsorbent. The capacity is simply the amount of adsorbate taken up by the adsorbent, per unit mass or volume of the adsorbent. The capacity will rely on the conditions such as fluid-phase concentration, temperature, pH and initial conditions of the adsorbent.

Adsorption capacity is an important parameter to determine the capital cost because it dictates the amount of adsorbent required, which also fixes the volume of the adsorber vessels. Adsorption isotherm is an important study to know the adsorbent .There is six classic isotherm types represented by different shapes of amount adsorbed versus relative pressure graph as illustrated in Figure 2.2. Various empirical forms are present to further evaluate the adsorbent. Beyond those, there are many other means to express adsorption capacity such as surface area, pore size

distribution, Iodine Number and Molasses Number. The latter two however are only used to describe activated carbons. As proposed by Duang D. Do (1998), the typical characteristic of ϒ-alumina effective surface area of alumina is between 200-300m^2/g with true density of 2.9-3.3 g/cm^3 and total porosity of 0.7-0.77.

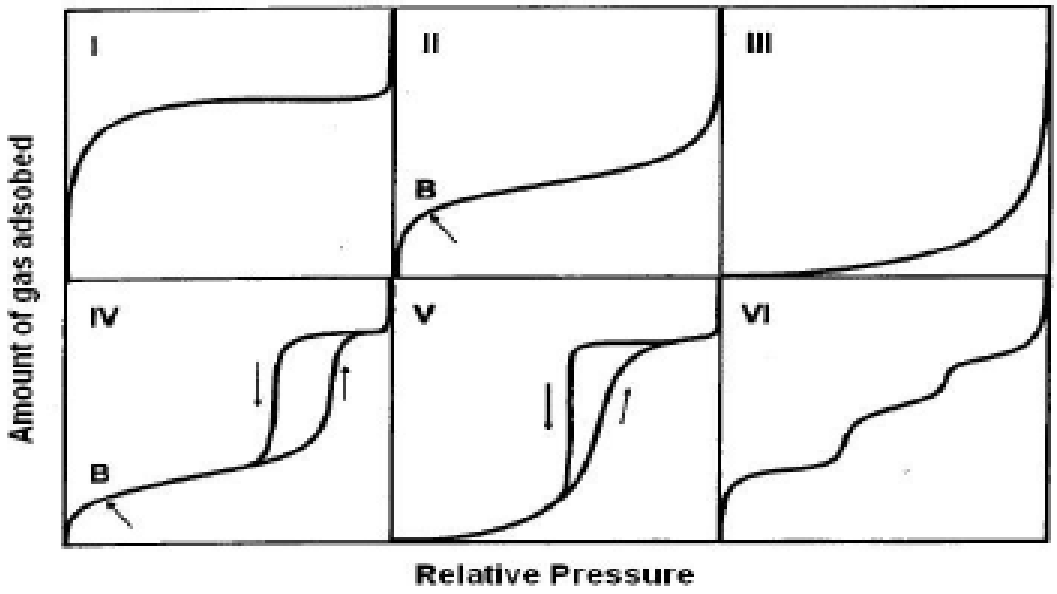

Figure 2.2: Types of sorption-isotherms

The study of adsorption capacity of the adsorbent is important to know the adsorbent's effectiveness. Several researchers have studied the adsorption activities of different adsorbent with different types of adsorbate, mostly pollutant (Sen, T. K., & Sarzali, M. V., 2008; Namasivayam, C., & Sangeetha, D., 2008; Kumar, U., & Bandyopadhyay, 2006).

The effects of various experimental parameters on kinetics and equilibrium adsorption of cadmium metal ion from its aqueous solution on aluminium oxide (Al_2O_3) have been investigated using batch adsorption experiments (Sen, T. K., & Sarzali, M. V., 2008).In this study, the authors had performed several experiments to elucidate the effectiveness of adsorbent used which is commercialized aluminium oxide (Al_2O_3) taken from Merck. It has been found that the amount of adsorption of metal ion increases with initial metal ion concentration, contact time, and solution

pH, respectively. It has also been found that amount of cadmium adsorption decreases with the amount of adsorbent and temperature, respectively.

2.4 Aluminium oxide (Al_2O_3)

Several approaches have been used to produce aluminium oxide (Al_2O_3) with different properties and applications (Belsky and co-workers, 1980; Zainab and Rozaina, 2008; Ji-Young Park and co-workers, 2002). Aluminium oxide (Al_2O_3) is widely used as an adsorbent and catalyst due to its mechanical strength and high surface area. The acid–base properties of aluminium oxide (Al_2O_3) are the main reason for its wide applications. A chemical species that behaves both as an acid and as a base is called amphoteric. This property depends upon the medium in which the species is investigated. Another reason for this interest is that the importance of adsorption on solid surfaces in many industrial applications in order to improve efficiency and economy. Therefore, it is essential to understand the mechanism and kinetics of adsorption, because the studies of adsorption kinetics are ultimately a prerequisite for designing an adsorption column (Hendrix and colleagues, 1990).

2.5 Precipitation method

Preparation of aluminium oxide (Al_2O_3) using convenience and simple precipitation method has long been studied. This method is proven to produce several mesoporous alumina using inexpensive inorganic aluminium salts with ammonium acetate as precipitating agent. In order to be used as fine chemical purification, catalyst, catalyst support and adsorbents, the alumina should have high specific surface areas and narrow pore size distribution. For example, the mesoporous alumina absorbent for purifying liquid crystal (LC) is about 100 times higher than the unit price of alumina .It is well known that undesirable cokes that formed during catalytic reactions can easily plugging the microspores thus disturbing the diffusion of reactant and product. Therefore, the conventional aluminium oxide (Al_2O_3) that composes of a mixture of macro, meso, and microspores in irregular sizes has been utilized. In addition, catalysts like existing aluminium oxide (Al_2O_3) which possesses wider pore-size distribution are prone to rapid deactivation (Zainab and Rozaina, 2008).

Preparation of alumina by the sol–gel technique from aluminium alkoxides is well established (Lewis and McNeese, 1986; N.Bahlawane and T.Watanabe, 2000). Hydrolysis of aluminium alkoxides at different processing conditions leads to the formation of alumina with different morphologies, surface areas and pore volumes. In the sol–gel processing of alumina from aluminium alkoxide, the use of chelating agents is essential to control the hydrolysis rate due to the relatively high reactivity of aluminium alkoxides. However, the extra reagent for modification in the sol–gel processing of alumina from aluminium alkoxide is expensive and thus limits the commercialization of high-purity alumina (Y.S Lin and G.Buelna, 2001).

Furthermore, modification of aluminium alkoxide with chelating agents for sol stabilization also is not suitable in the preparation of alumina thin films due to the high weight loss during the calcinations and consequently causes cracks formation. The wet particles extracted from the resultant solution need to be sequentially washed with cold water, warm water and alcohol to remove remnant oil and ammonia. The washing step is not economically feasible since it requires a large amount of washing solvent and also results in a loss of up to 25% of aluminium oxide (Al_2O_3). Elimination of this step is highly desired as this will minimize the generation of solvent waste, increase the efficiency of material utilization, simplify the process and reduce the costs (Q.Liu and co-workers, 2007). To decrease the cost of fabricating mesoporous alumina, inexpensive inorganic salt raw materials have been used to replace aluminium alkoxide as aluminium precursor.

Zainab and Rozaina (2008) applied nitric acid, acetone and ultrasonication treatments in simple precipitation method to synthesize alumina that will primarily use as a catalyst and also adsorbent. However,the added steps did not give significant difference in the pore distribution and BET surface area of the alumina obtained by both acid and acetone treatments while ultrasonication contribute in small increment in surface area and porosity of the catalyst.

Calcinations are required to convert the aluminium hydroxide into aluminium oxide (Al_2O_3). The calcinations temperatures for various applications are studied to know

the effect of different calcinations temperature to phase transformation and particle size of the final products. Characterization testings has been done to adsorbent to know the behaviour of adsorbent at temperatures of 700,900 and 1100^{o}C. The ideal temperature for calcinations is at temperature 700^{o}C.Generally, size of the particles will be larger with increasing temperature.However, control of the morphology and the particle-size distribution in the a-Al_2O_3 powders can be accomplished by reducing the phase transformation temperature because the high-temperature annealing induces a sintering process (Ji-Young Park and co-workers, 2002).

CHAPTER 3

3.0 METHODOLOGY

3.1 Overview of the Project

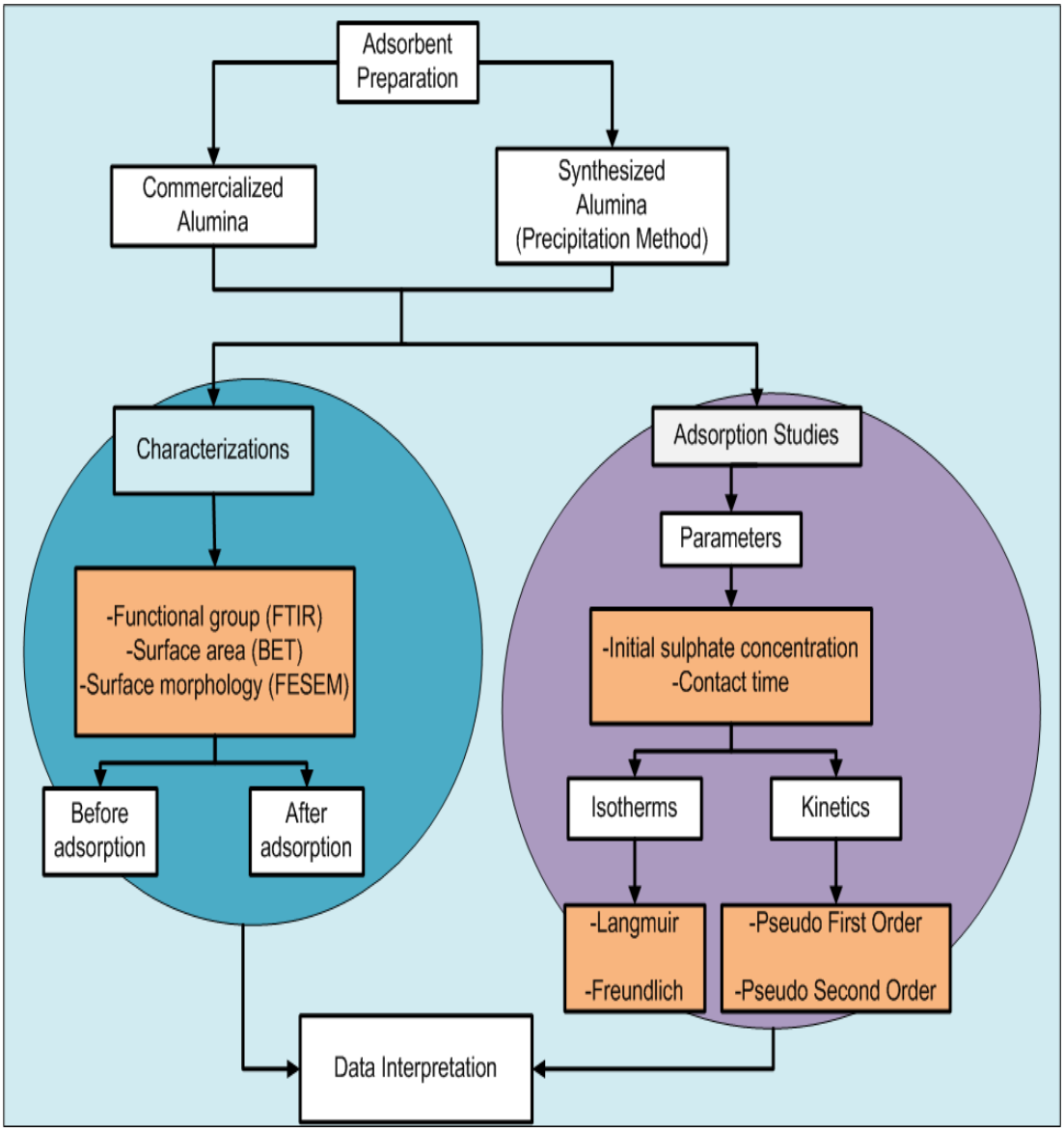

Figure 3.1: Flow chart of Analytical Works

3.2 Experimental

3.2.1 Materials

Aluminium chloride hexahydrate (99%) and ammonium hydroxide (NH_3 25%) were purchased from R & M Chemicals.Commercialized aluminium oxide (Al_2O_3) as control adsorbent and sodium sulphate that is used to prepare synthetic aqueous stream was obtained from Merck Chemical.The chemicals were used as received without further purification. The water used in this work was distilled water.For characterization of the adsorbent , FESEM,FTIR,XRD and TGA equipment were used while sulphate concentration was measured using DR/4000 UV-Vis Spectrophotometer.

3.2.2 Preparation of aluminium oxide (Al_2O_3) particles.

Figure 3.2 shows steps taken in Precipitation method to synthesize aluminium oxide (Al_2O_3).

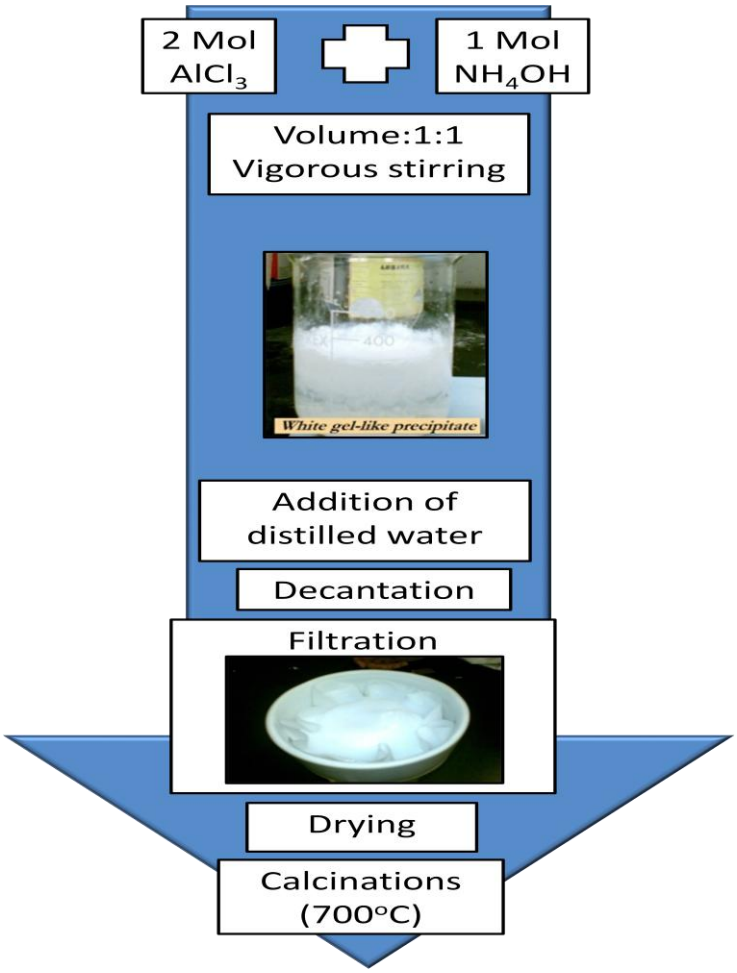

Figure 3.2: Flow chart of Precipitation method

The 2-M aluminium chloride hexahydrate was added into 1-M of ammonium hydroxide solution.Under vigorous stirring,the ammonium hydroxide solution acted as precipitating agent.In this step, the white gel-like precipitate was generated instantly. The supernatant was removed from the precipitate by decantation.The precipitate was washed three times using distilled water to remove the impurities. Coarse powder is obtained by filtering then dried in the common convection oven at temperature of 120^{o}C for about 3-4 hour until complete moisture removal.Then,the sample was calcined to get Al_2O_3 particles at 750 for 2 hour in air atmosphere. After heat treatment, the Al_2O_3 powder was ground and subsequently sieved using 500 micrometer mesh to obtain particles with same range of size.Finally, the prepared sample was sent to BET FESEM, FTIR, XRD and TGA for characterizations.

3.2.3 Characterization studies

i. Brunauer, Emmett and Teller (BET)

Surface area and porosity are important characteristics, capable of affecting the quality and utility of many materials. For this reason it is important to determine and control them accurately. Likewise, knowledge of porosity and surface area are frequently important keys in understanding the structure, formation and potential applications of different natural materials. The most widely used technique for estimating surface area is called BET method (Brunauer, Emmett and Teller, 1938). The BET surface areas and pore volumes were estimated from nitrogen adsorption and desorption isotherm data obtained using Micromeritics ASAP2405 volumetric adsorption analyzer

ii. FTIR (Fourier Transform Infra Red)

The FTIR is widely used to determine the structure of organics compound. Infrared can identify the presence of certain functional groups within a molecule. FTIR technique is an analytical method used to identify the chemical structure of many inorganic chemical and also organics materials or compound. Most FTIR units operate within the range of 400-4000 cm^{-1} wave number. The wave number is used as these numbers are directly proportional to energy. Functional group tends to adsorb a photon of infrared radiation. Hence, the energy increase and it is associated with bond vibrations involving in the stretching and bending of bonds. FTIR analysis can be applied to small quantities of materials, whether solid, liquid, or gaseous. The equipment being used in this study was Perkin Elmer (1600 series) spectrometer using the KBr wafer technique**.**

iii. Scanning Electron Microscopy (FESEM)

Field Emission Scanning Electron Microscope (FESEM) creates the

magnified images by using electrons. FESEM shows 3-dimensional images at much higher magnifications. The images are very detailed. The images created without light waves are rendered black and white. It can be used to estimate the pore size of the alumina quantitatively.

3.2.4 Adsorption studies

i. Effect of initial sulphate concentration

The effect of initial sulphate concentration on the amount of sulphate ion adsorbed was obtained by contacting 250mL of different initial concentrations of sulphate ion solution with 30mg of aluminium oxide using water bath shaker at 25.7 $^{\circ}$C for 3 hour at a constant speed of 250 rpm.The initial concentration of the solution was 10mg/L followed by 20mg/L,30mg/L,40mg/L and 50mg/L. The initial solution of pH was at about 6.70. At each time interval, the samples were filtered and the supernatant solution was analyzed for its concentration using DR/4000 UV-Vis Spectrophotometer following Sulfa Ver 4 Method.The same procedure was also conducted to commercialized aluminium oxide (Al_2O_3).

ii. Adsorption Kinetics

The kinetics of metal ion adsorption were carried out using 30ppm sulphate ion concentrations at a fixed pH on adsorbent as per earlier experimental procedure. The only difference was that thr samples were collected and analyzed at regular intervals during adsorption process.

iii. Adsorption equilibrium

For equilibrium isotherm studies, sulphates ion solutions of different initial concentrations were taken in batches of 250mL solutions in a series of 500mL conical flasks. 0.5 g of Al_2O_3 was added to each bottle

and samples were inserted in a water bath shaker for a period of 1 h. After equilibrium,each sample was analyzed for left out equilibrium sulphate (SO_4^{2-}) oncentration as per earlier section.

CHAPTER 4

4.0 RESULTS AND DISCUSSIONS

This chapter presents the results and discussions for main aspects of the research work, namely the adsorbent characterizations and the adsorption behavior of the synthesized alumina towards sulphate ions at different conditions. Figure 4.1 shows the synthesized alumina that has been prepared using Precipitation method as discussed earlier. The alumina is sieved using mechanical sieve with 500µm diameter of sieve. Therefore the particle size of synthesized alumina is believed to be in a range of 500-1000 µm.The characterization and adsorption results obtained are compared with the commercialized alumina taken from Rohm and Hass.

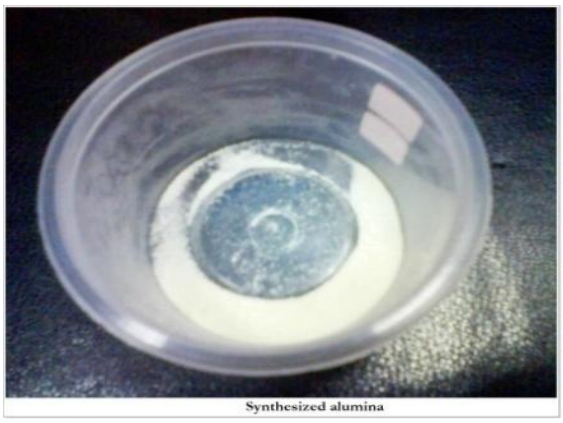

Figure 4.1: Picture of synthesized alumina

4.1 Characterization of the Adsorbent

4.1.1 Fourier Transform Infra Red (FTIR)

FTIR technique is an analytical method used to identify the chemical structure of many inorganic chemical and also organics materials or compound. Infrared can also identify the presence of certain functional groups within a molecule. Figure 4.2 and Figure 4.3 shows the results of FTIR obtained for synthesized and commercialized alumina.

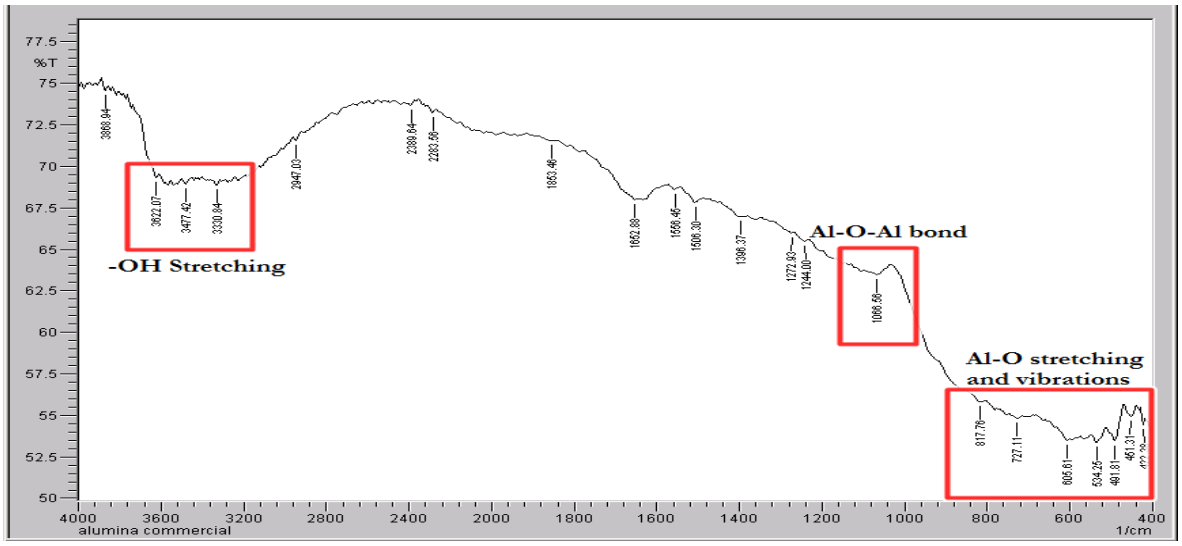

Figure 4.2: Infrared Spectra of Commercialized Alumina

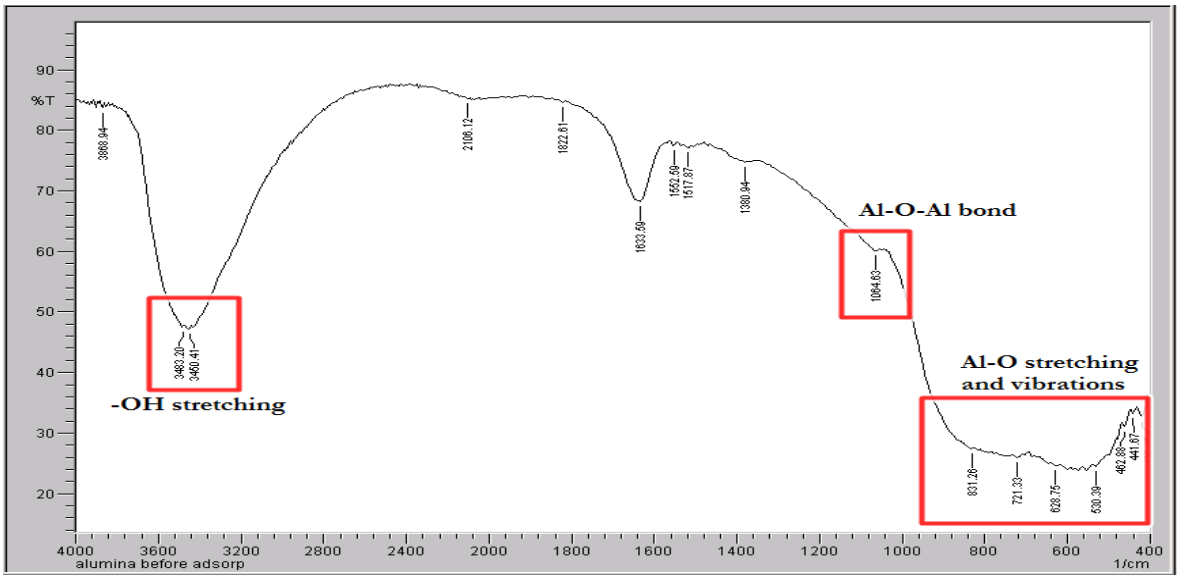

Figure 4.3: Infrared Spectra of Synthesized Alumina

Commercialized and synthesized alumina spectrums are similar and show no obvious differences between each other. For both types of alumina, the broad band at 3200-3700 cm^{-1} corresponds to the stretching vibration of the –OH group bonded to Al cation and peak at 1633 cm^{-1} corresponds to water of hydration. The peak corresponding to 1065 cm^{-1} was assigned to Al–O–Al symmetric bending stretching vibrations while bands at 462 and 617 cm^{-1} are attributable to bending and stretching modes of AlO_6. Peak at 721 cm^{-1} and 831 cm^{-1} may be due to Al–O stretching vibrations (Zainab and Rozaina, 2008).

As shown in Figure 4.4 below, it can be concluded that FTIR analysis of synthesized alumina exhibit FTIR spectra shown by boehmite (γ-AlO (OH)) (S.Music et al., 1995).

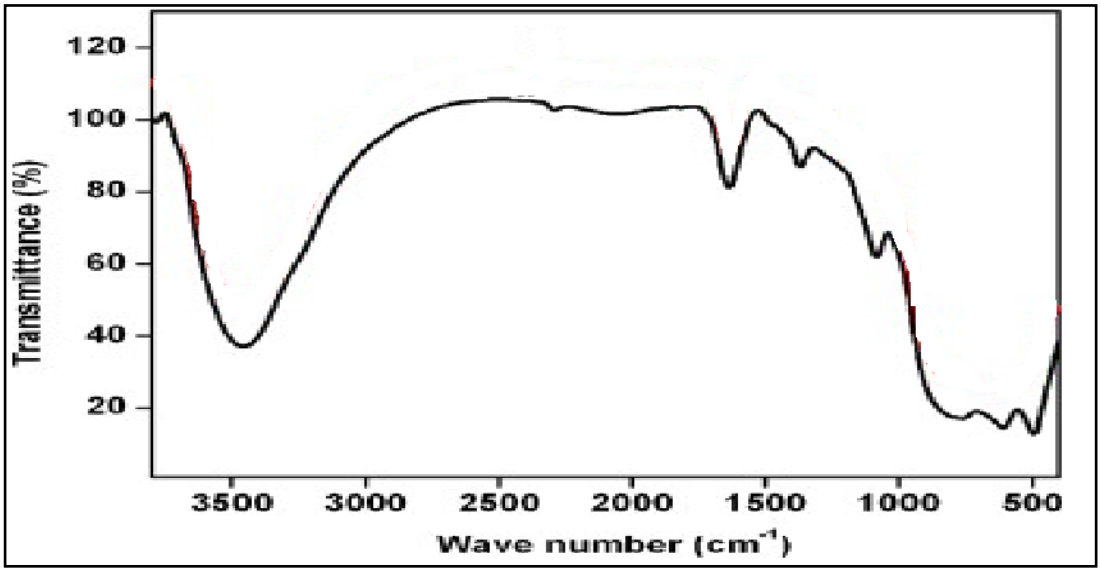

Figure 4.4: Infrared Spectra of Boehmite

As stated by S.Music and co-workers (1995), boehmite has the potential to be formed via precipitation from aqueous solutions.Boehmite (y-AlOOH) was often used as the starting material for preparation of aluminium oxide ceramics. For example, boehmite prepared by a sol-gel procedure was used as the starting material in production of ceramic membranes by the addition of small amounts of Lanthanum (La^{3+}) ions to boehmite in the colloidal state.

4.1.2 Brunauer, Emmett and Teller (BET)

The BET method is based on adsorption of gas on a surface.The amount of gas adsorbed at a given pressure allows determination of the surface area. The value for the BET surface area is calculated using values determined for the gradient and intercept of the BET transformation plot together with the sample mass and well-defined physical constants, as shown in Table 4.1.

BET Surface Area Report	
BET Surface Area:	166.0590 ± 0.4221 m^2/g
Slope:	0.025994 ± 0.000066 g/cm^3 STP
Y-Intercept:	0.000221 ± 0.000010 g/cm^3 STP
C:	118.484751
Qm:	38.1464 cm^3/g STP
Correlation Coefficient:	0.9999775
Molecular Cross-Sectional Area:	0.1620 nm^2

Table 4.1 :Typical Surface Area Result For Synthesized Alumina

Figure 4.5 and Figure 4.6 presents the N_2 adsorption-desorption isotherm and BJH pore size distributions for synthesized sample.From the graph in Figure 4.5, it shows that the sample exhibited a type IV adsorption isotherm with a H1 adsorption–desorption hysteresis loop. This adsorption characteristic is usually attributed to adsorption in mesopores, which are classified by IUPAC as pores of diameter 2–50 nm (Soonki Kang,2002).Type IV adsorption isotherm represents favourable adsorption.

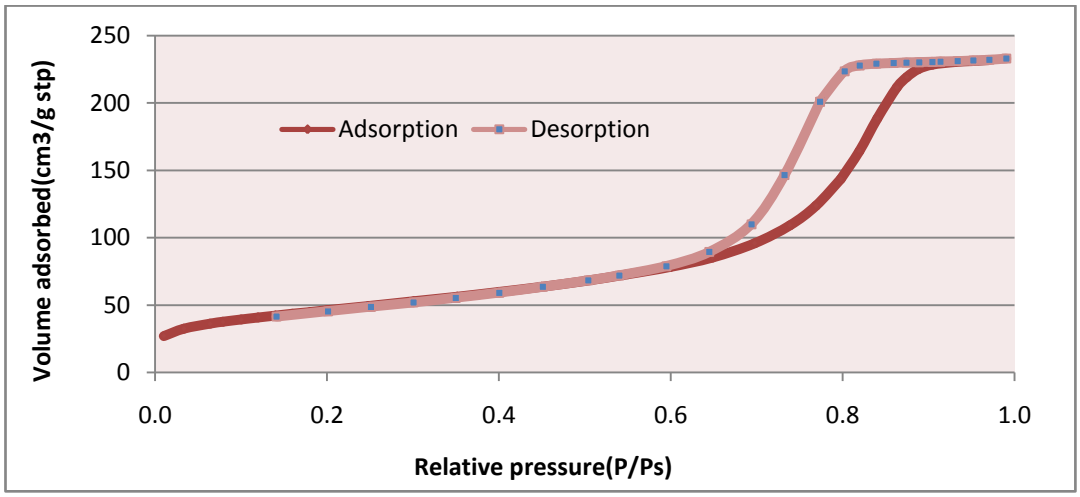

Figure 4.5:N_2 adsorption-desorption plots of synthesized alumina

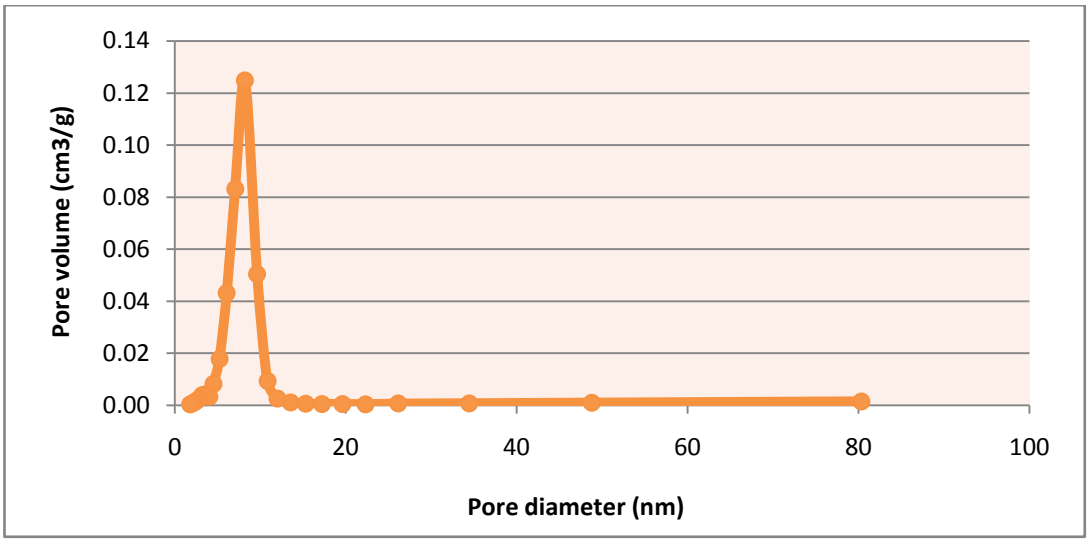

Figure 4.6: BJH pore size distribution of synthesized alumina

The result from BJH pore size distribution of synthesized alumina clearly illustrate that the synthesized sample exhibits a narrow pore size distribution centered at 8.2 nm. Higher BET surface area (166 m^2 /g) as compared to commercial y-alumina (BET surface area~90-100 m^2/g) and high pore volume with average pore diameter 8.6 nm indicates that the synthesized alumina will have better adsorbent characteristics than commercialized alumina (Zainab and Rozaina, 2008). The BET linear plot results in perfect straight line as illustrated in Figure 4.7 showing that the solids do not contain large amount of micropores or supermicropores and mesopores are rather large (A.W.Marczewski ,2002).

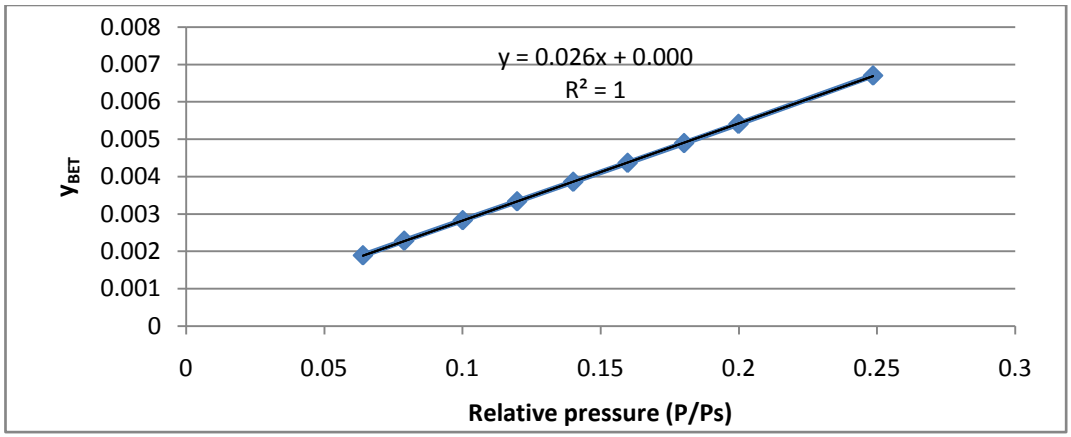

Figure 4.7 : Adsorption isotherm of N_2 on synthesized alumina-BET linear plot

4.1.3 Scanning Electron Microscopy (FESEM)

Figure 4.8 and Figure 4.9 show the particle morphology of synthesized and commercialized alumina. The commercialized alumina shows formation of irregular shapes particles with wide size distribution. The pore structure of the commercialized alumina cannot be clearly identified from the FESEM obtained. It shows a long opening of pore like a crack. The observation FESEM shown by synthesized alumina in Figure 4.8 and Figure 4.9 clearly shows the difference in particle morphology between synthesized and commercialized alumina. Morphology of synthesized alumina shows pores with quite similar sizes that are interconnected to each other.

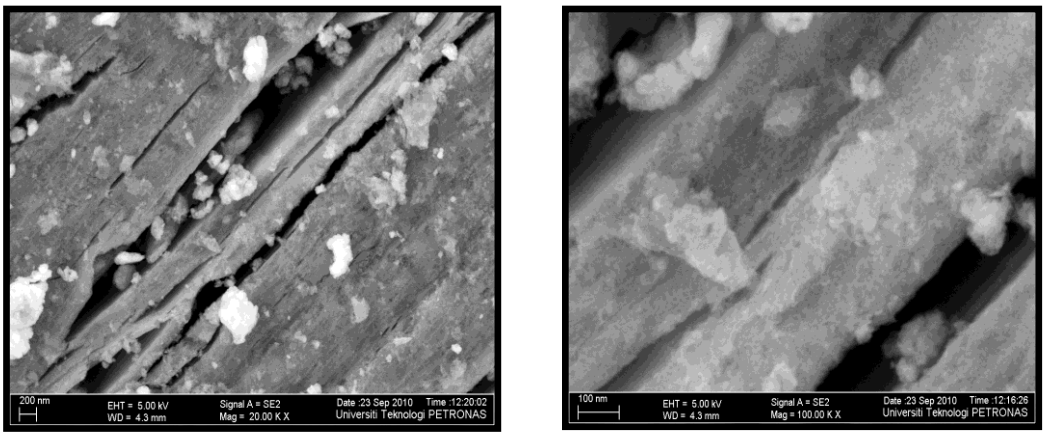

Figure 4.8: FESEM micrograph with magnification 20K and 100K for the commercialized alumina before adsorption.

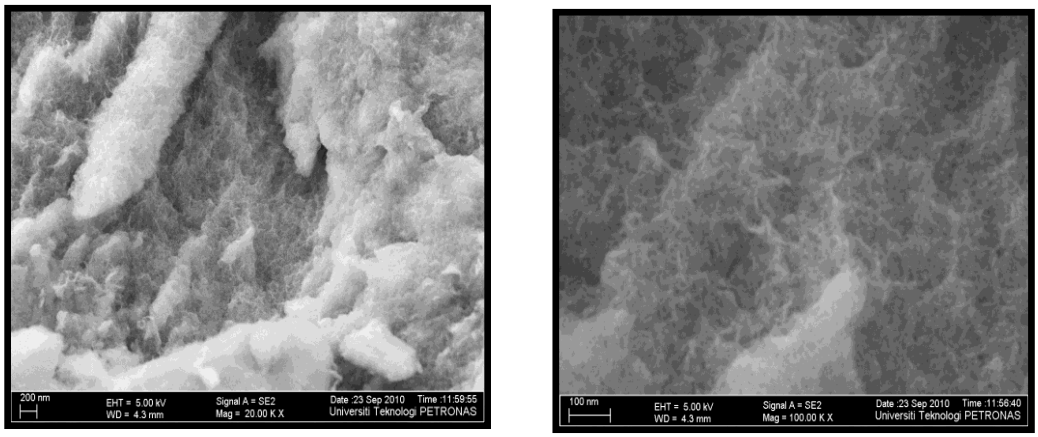

Figure 4.9: FESEM micrograph with magnification 20K and 100K for the synthesized alumina before adsorption

4.2 Characterization of synthesized alumina after adsorption with sulphate ions

4.2.1 Fourier Transform Infra Red (FTIR)

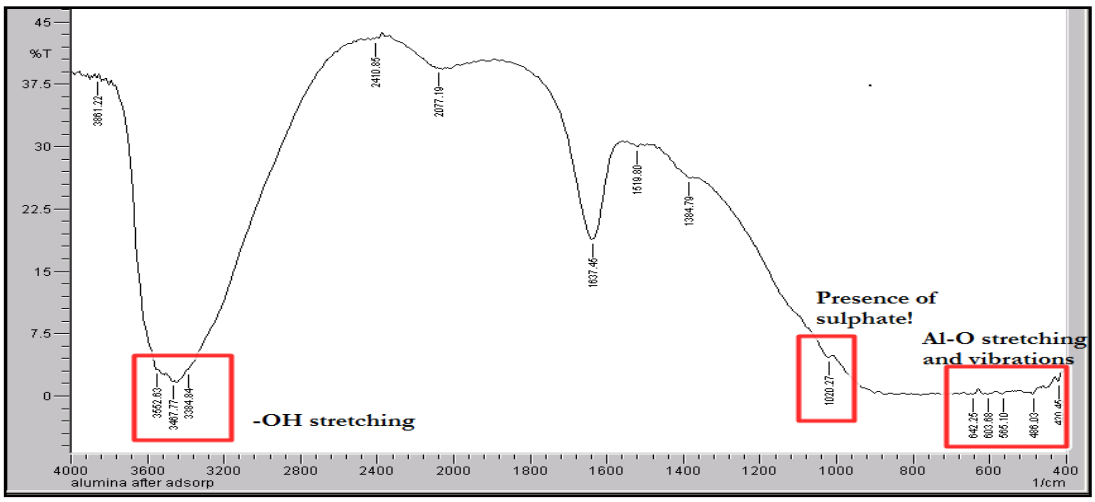

Figure 4.10: Infrared spectra of synthesized alumina after adsorption

From Figure 4.10, new peak is observed at 1020 cm^{-1} for synthesized alumina after adsorption. As a free anion in solution, sulphate has tetrahedral symmetry and belongs to the point group three dimensioanal as shown in Figure 4.11. For this symmetry, only one broad peak at approximately 1100 cm^{-1} due to the triply degenerate C_{3v} band is usually observed.Since outer-sphere complexes retain their waters of hydration and form no surface chemical bonds, it can be expected that the symmetry of outer-sphere sulphate complexes would be similar to aqueous sulphate.The range of IR spectra shown by various arrangement of sulphate is in between 975-1250cm^{-1} (M. Weber and F. C. Nart ,1996).

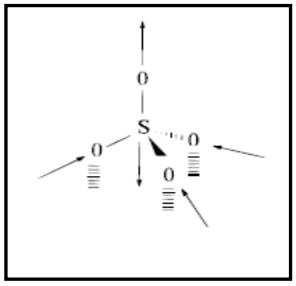

Figure 4.11: Surface selection rule allowed sulphate stretching vibration for adsorbed sulphate ion under C_{3v} symmetry.

4.2.2 Scanning Electron Microscopy (FESEM)

The differences between surface morphology of the synthesized alumina before and after adsorption are shown in Figure 4.12 and Figure 4.13.From the pictures, it is confirmed that the adsorption mechanism has occurred. The pores of alumina after adsorption have been covered. Less amount of pores are observed after adsorption.

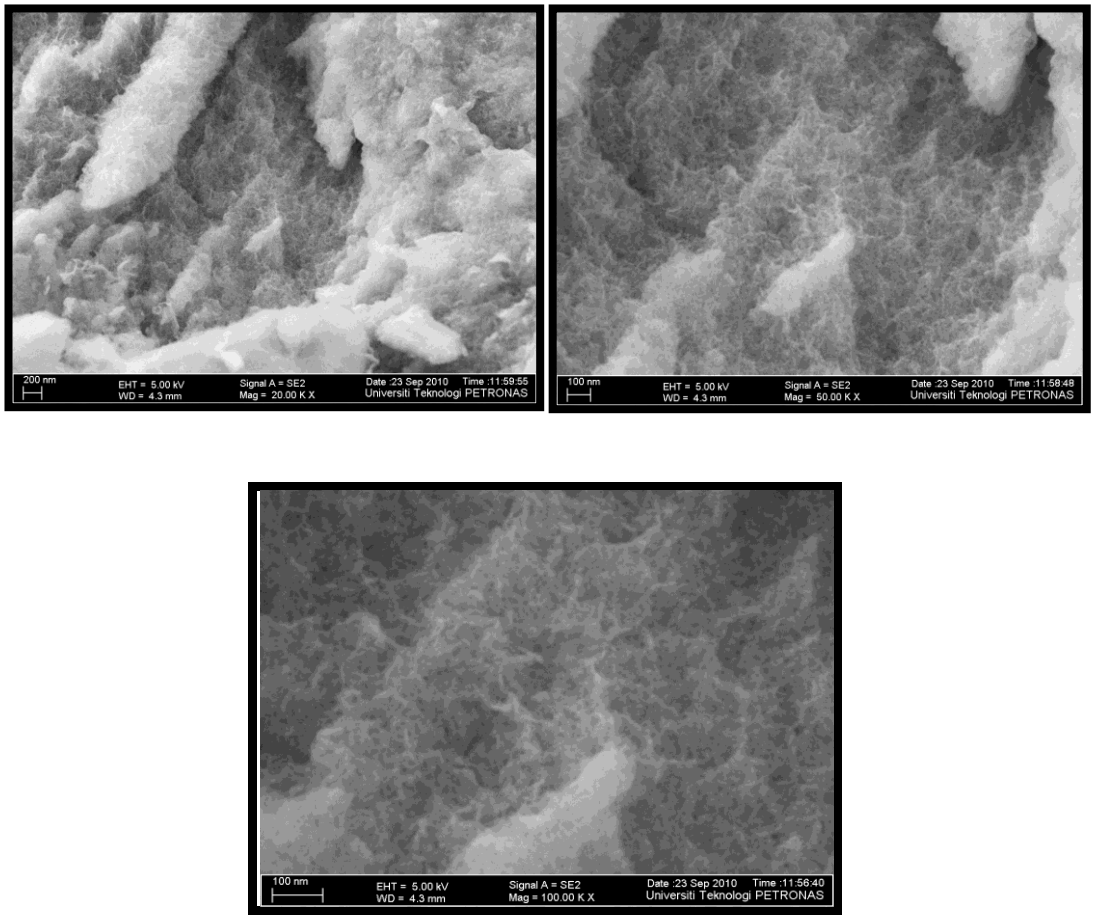

Figure 4.12: FESEM micrograph with 20K, 50K and 100K magnifications of the synthesized alumina before adsorption.

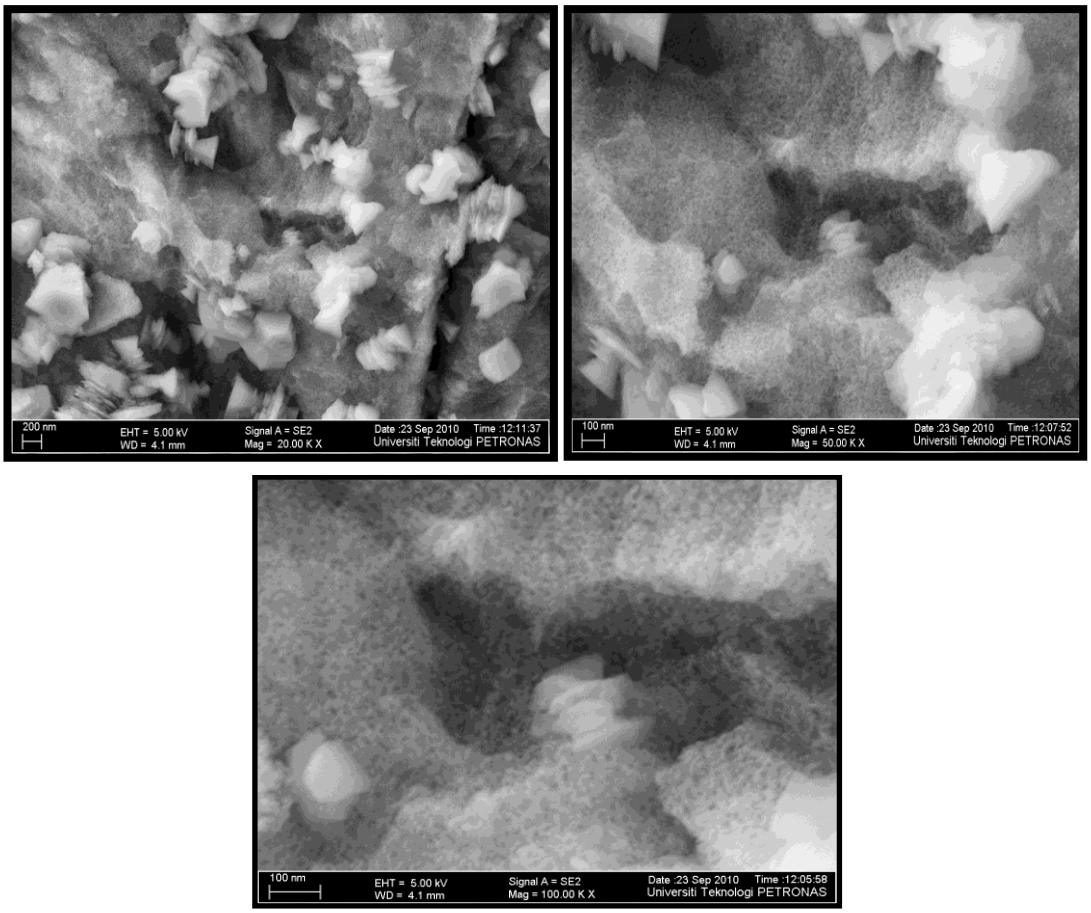

Figure 4.13: FESEM micrograph of the synthesized alumina with 20K, 50K and 100K magnifications after adsorption

4.3 Effect of contact time

Adsorption of sulphate using both types of adsorbent (synthesized alumina and commercialized alumina) were measured at a given contact time for five different initial sulphate concentrations from 10 to 50 mg/L.The choice of concentration was based on the typical concentration ranges for sulphate constituents in untreated domestic waste-water. Concentrations of 20mg /L, 30mg/L and 50mg/L in waste-water are classified as strong, medium or weak respectively. Figure 4.14 shows that percentage of sulphate removal increases with increasing contact time for all initial sulphate ions concentration for synthesized alumina.In other words, the amount of sulphate adsorbed to synthesized alumina increases with increasing contact time.Equilibrium is attained within 45 minutes.Same adsorption behaviour is shown by commercialized alumina as ilustrated in Figure 4.15. The equilibrium time for

commercialized alumina is slightly higher than synthesized alumina which is within 50 minutes.The average percentage of sulphate removal (when equilibrium is achieved) for different initial sulphate concentration is 51.3% for synthesized alumina and 52.8% for commercialized alumina.

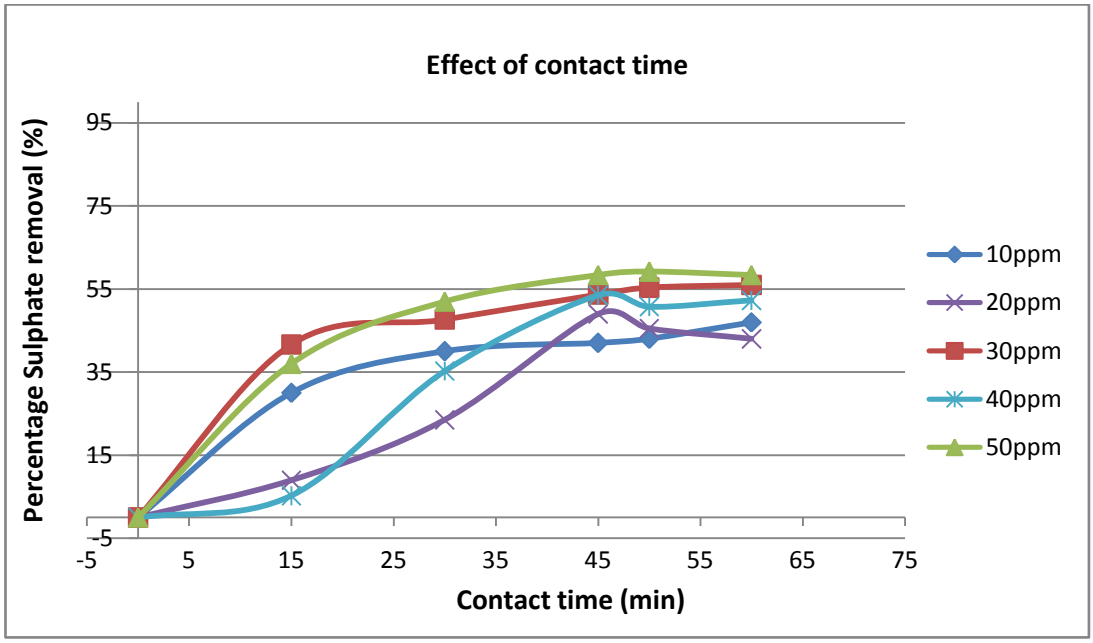

Figure 4.14: Effect of Contact Time for synthesized alumina

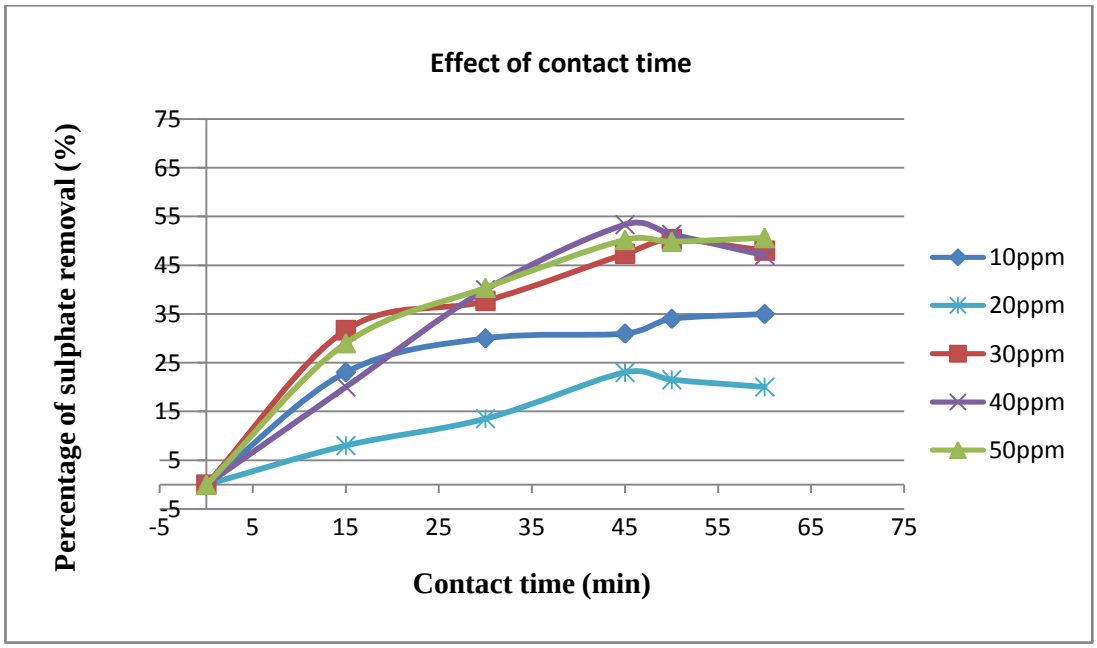

Figure 4.15: Effect of Contact Time for commercialized alumina

The adsorption is starting to increase steadily at the initial 5 minutes of experiment.It indicates that initially, the active surface sites of the adsorbent are rapidly occupied with the sulphate ions. This is because in the beginning, active surface sites are vacant and readily available to occupy sulphate ions. The same trend continues until equilibrium is attained at 45 and 50 minutes for synthesized and commercialized alumina respectively. However, for commercialized alumina, there is slight fluctuation observed before equilibrium at initial sulphate concentration of 40ppm and 20ppm.The reasons might be because of UV-vis equipment failure or calibration errors during experiment was conducted. Lesser sulphate ions were being adsorbed onto the adsorbent giving a low percentage of sulphate removal when reaching equilibrium point. This is probably due to slower diffusion of solute onto the interior of the adsorbent as the surface of adsorbent is rich with sulphate ions. The trend of the adsorption curve is getting flatter and almost a straight line indicating that there is barely any adsorption after equilibrium.

4.4 Effect of initial sulphate concentrations

A series of batch experiments was conducted for various initial sulphate concentrations to establish the adsorption isotherms.This parameter is investigated under the specified conditions; initial pH of 6.7; contact time of 45 min; adsorbent dosage of 30 mg; and temperature of 25.7^{o}C using water bath shaker. Figure 4.16 shows initial adsorbate concentration versus percentage of sulphate removal for synthesized alumina while Figure 4.17 shows initial adsorbate concentration versus percentage of sulphate removal for commercialized alumina.

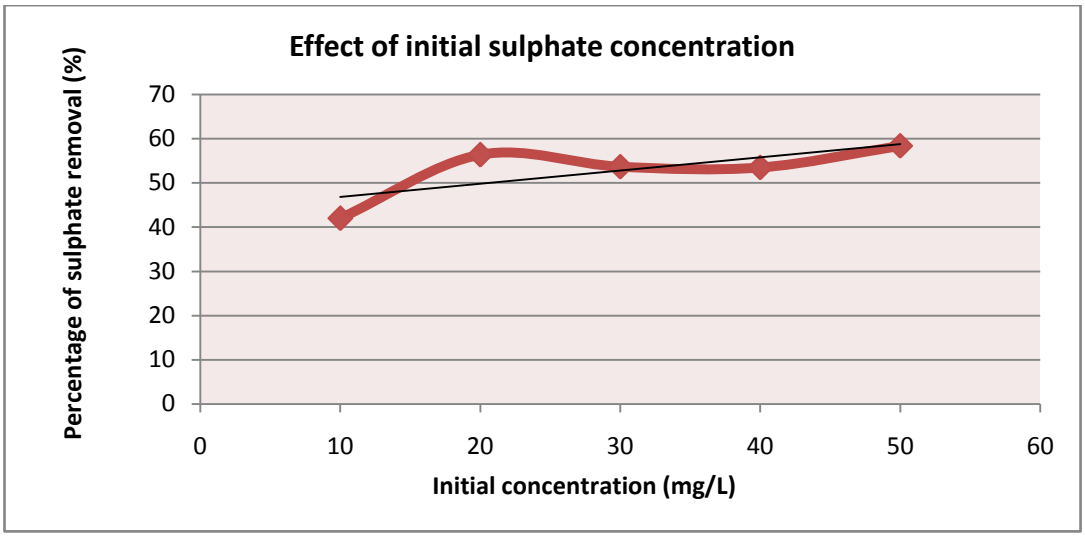

Figure 4.16: Effect of initial sulphate concentrations on sulphate ion adsorption using synthesized alumina

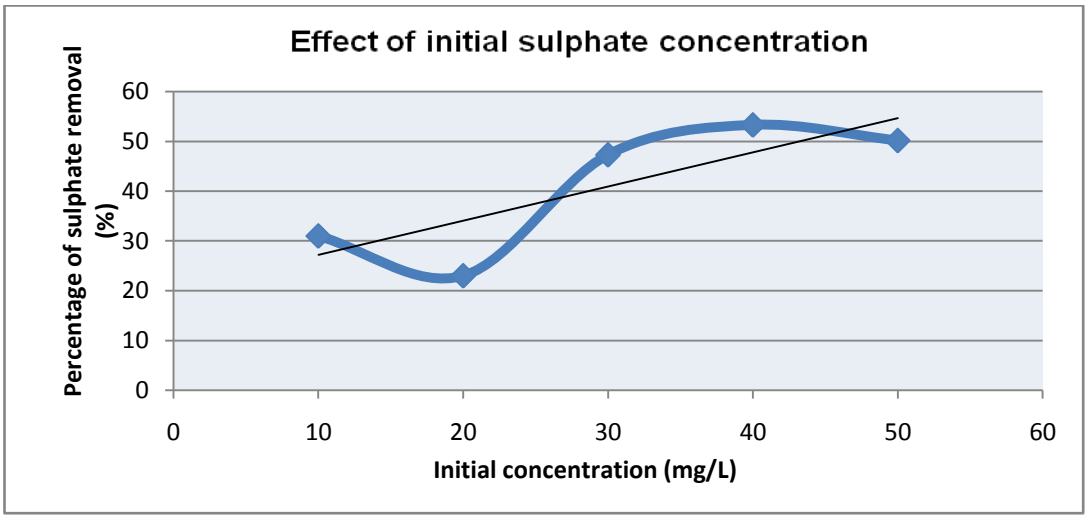

Figure 4.17: Effect of initial sulphate concentrations on sulphate ion adsorption using commercialized alumina

4.5 Equilibrium study

Both Langmuir and Freundlich isotherms graph are plotted to see which isotherm best represent the adsorption.As shown in Figure 4.18 and Figure 4.19, the Freundlich and Langmuir models were fitted to the experimental data obtained from synthesized alumina with relatively good applicability. The fitted parameters for these two models are summarized in Table 4.2 and indicates that the adsorption of sulphate by synthesized alumina is assumed to be favorable and single-layered.

For the commercialized alumina,the adsorption is best represent by Langmuir model shown in Figure 4.18 with R^2 of 0.909.The best fitted isotherm is selected based on value of R^2 which is goodness of fit criteria computed by linear regression (E. Voudrias et al.,2001).

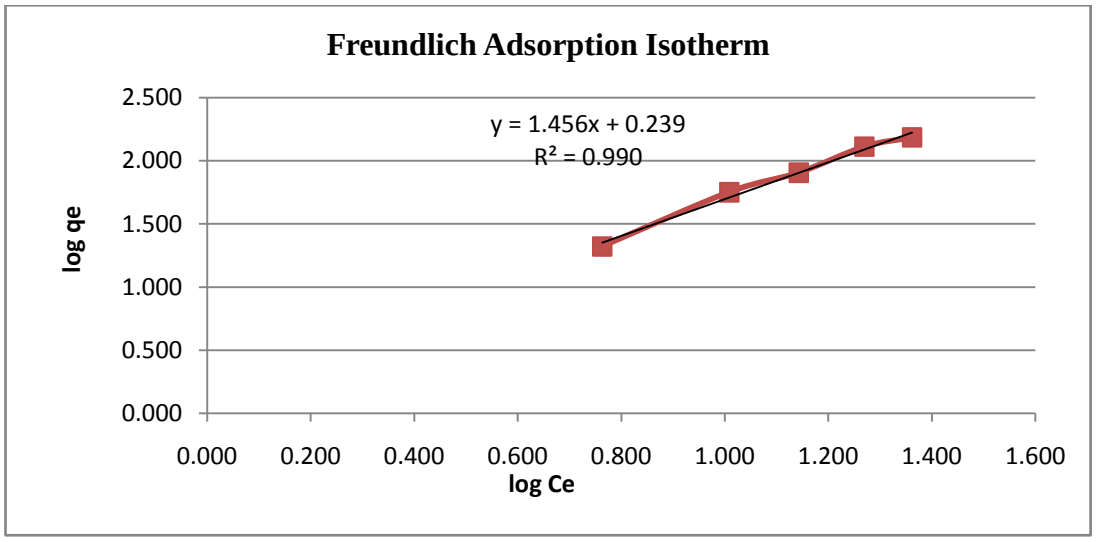

Figure 4.18:Freundlich Isotherm for synthesized alumina

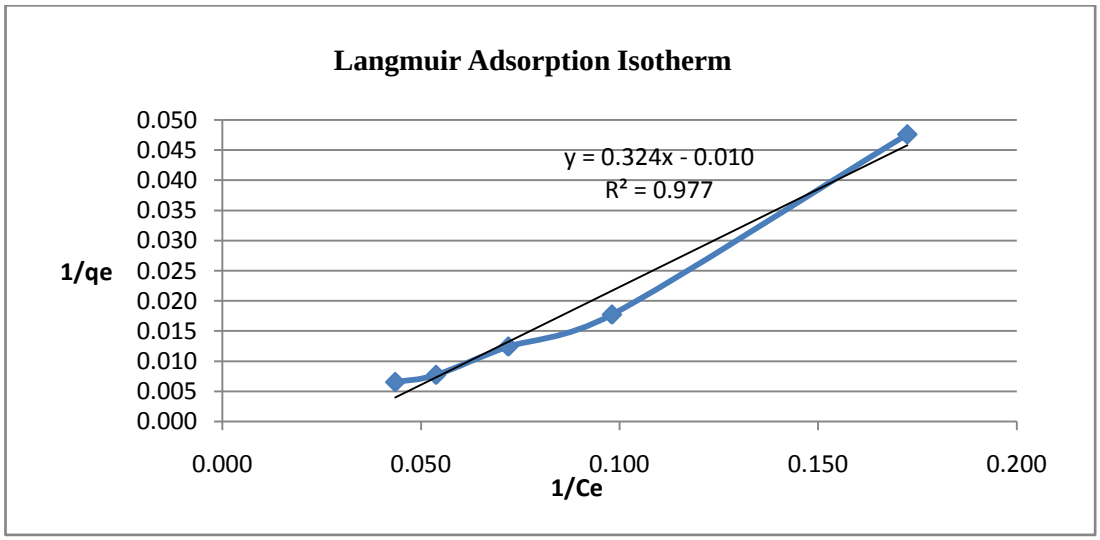

Figure 4.19 :Langmuir Isotherm for synthesized alumina

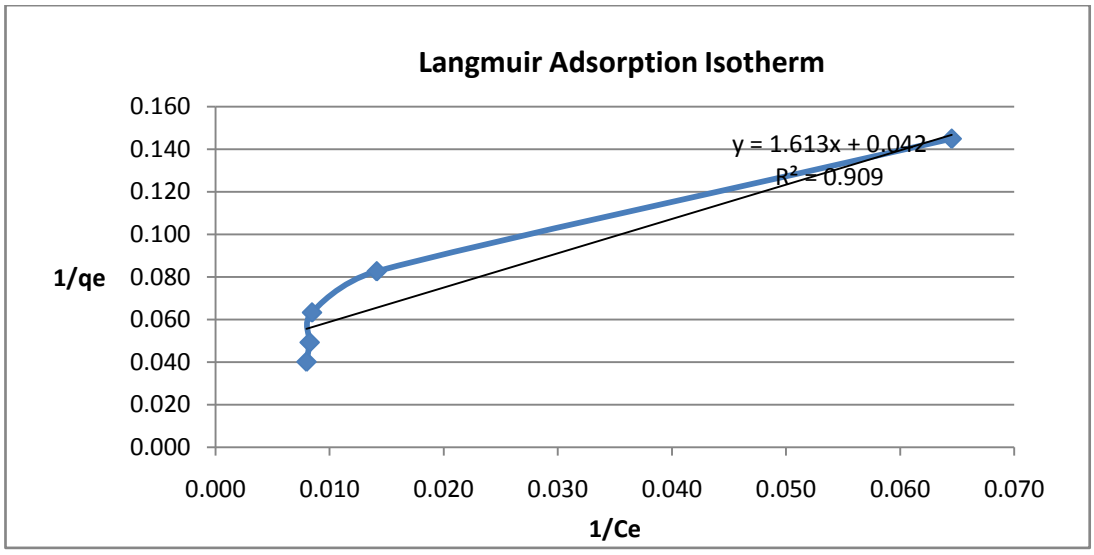

Figure 4.20 :Langmuir Isotherm for commercialized alumina

Langmuir (1918) was the first to propose a coherent theory of adsorption onto flat surface based on kinetic viewpoint. There is a continual process of bombardment of molecules onto the surface and a corresponding evaporation (desorption) of the molecules from the surface to maintain zero rate of accumulation at the surface at equilibrium. The surface of adsorption that follows Langmuir model is assumed to be homogenous that indicates surfaces energy is constant over all sites. Adsorbed atoms or molecules are adsorbed at definite and localized sites where only one atom/molecule can accommodate those sites.

On the other hand, Freundlich model assumed that surface of adsorption is heterogeneous in the sense that the adsorption energy is distributed. Surface topography is patchwise where sites having same adsorption energy are grouped together into one patch. Adsorption energy can be defined as the energy of interaction between adsorbate and adsorbent. However, each patch is independent from each other, that there is no interaction between patches. Freundlich further assumed that on each patch, only one adsorption site can be adsorbed adsorbate molecule. Hence, the Langmuir model may be applicable for the description of equilibria of each patch (Duang D. Do, 1998).

Langmuir isotherm can be represented by Equation 4.1.From the Langmuir Adsorption Isotherm graph, the value of two parameters which are constant related to binding energy of sorption system, K_L and maximum adsorption capacity, q_m can be identified from the intercept and slope of the plot. Freundlich isotherm follows the correlation as shown in Equation 4.1.The value of K_f and *n* in Freundlich correlation will indicate the capacity and intensity of the adsorption, respectively.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L}\frac{1}{C_e} \qquad \text{(Eq. 4.1)}$$

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad \text{(Eq. 4.2)}$$

Table 4.2 shows the result of Langmuir and Freundlich correlations for both synthesized and commercialized alumina. The result shows that synthesized alumina can be best represented by both Langmuir and Freundlich models. The maximum adsorption capacity of sulphate and constant related to binding energy of the sorption system is calculated which are 100 mg/g and 0.031 respectively for synthesized alumina and 23.8mg/g and 0.026 for commercialized alumina.

Table 4.2: Langmuir and Freundlich constants for both synthesized and commercialized alumina

Alumina	**Freundlich Isotherm**			**Langmuir Isotherm**		
Constants	**K_f**	**n**	**R^2**	**K_L**	**q_m**	**R^2**
Synthesized	1.734	0.687	**0.990**	0.031	100	**0.977**
Commercialized	0.828	0.599	**0.869**	0.026	23.8	**0.909**

4.6 Kinetic Study of Adsorption

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo first order and pseudo second order equations are applied to model the kinetics of sulphate adsorption onto synthesized and commercialized Aluminum Oxide (Al_20_3).The pseudo first order rate equation is given as :

$$\log(q_e - q_t) = logq_e - \left(\frac{k_{ad}}{2.303}\right) t \qquad \text{(Eq. 4.3)}$$

where q_t and q_e are the amount adsorbed (mg/g) at time, t and at equilibrium respectively and k_{ad} is the rate constant of pseudo first order adsorption process (min^{-1}).Straight line plots of log (q_e-q_t) against t were used to determine the rate constant, k_{ad} and correlation coefficient, R^2, for different sulphate concentrations are shown in Figures 4.21 and 4.22.

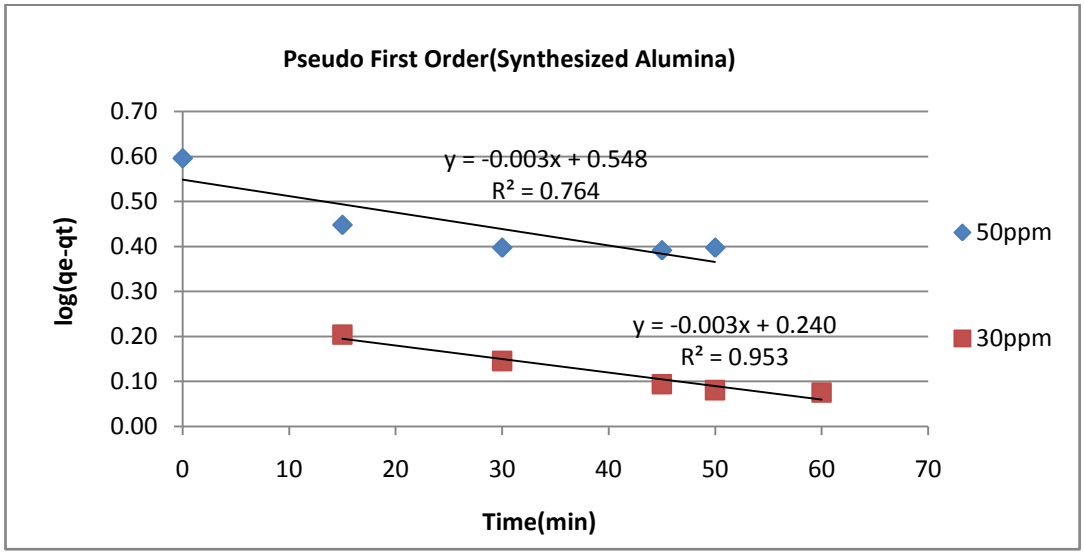

Figure 4.21: Pseudo first order Reaction for SO_4^{2-} Ions Adsorbed onto Synthesized Alumina at Different Concentrations

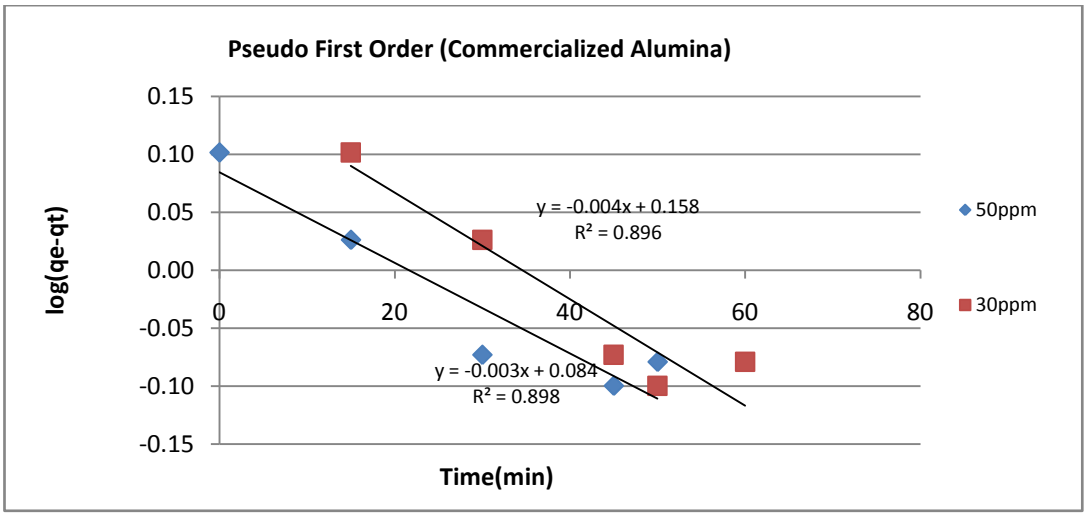

Figure 4.22: Pseudo first order Reaction for SO_4^{2-} Ions Adsorbed onto Commercialized Alumina at Different Concentrations.

The pseudo second order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{h} + \left(\frac{1}{q_e}\right) t \qquad \text{(Eq. 4.4)}$$

Where $h=kq_e^2$ (mg g $^{-1}$ min^{-1}) can be regarded as the initial adsorption rate as t approaching 0 and k is the rate constant of pseudo second order adsorption(g mg $^{-1}$ min^{-1}).The t/q_t versus t graph is plotted to determine the constants q_e, k *and* h. The plots of the linearized form of the pseudo second order reaction at different SO_4^{2-} concentrations for synthesized and commercialized alumina are shown in Figures 4.23 and 4.24.

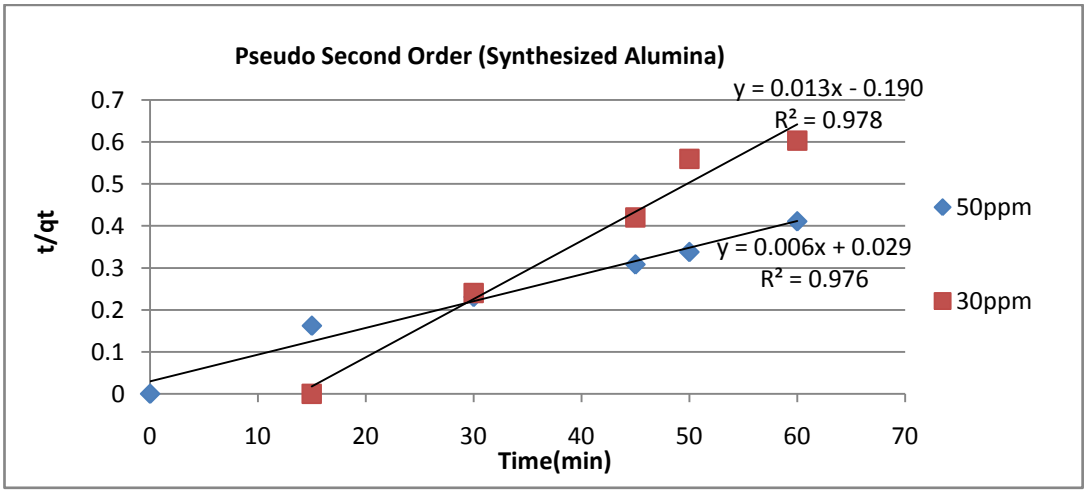

Figure 4.23: Pseudo Second order Reaction for SO_4^{2-} Ions Adsorbed onto Synthesized Alumina at Different Concentrations.

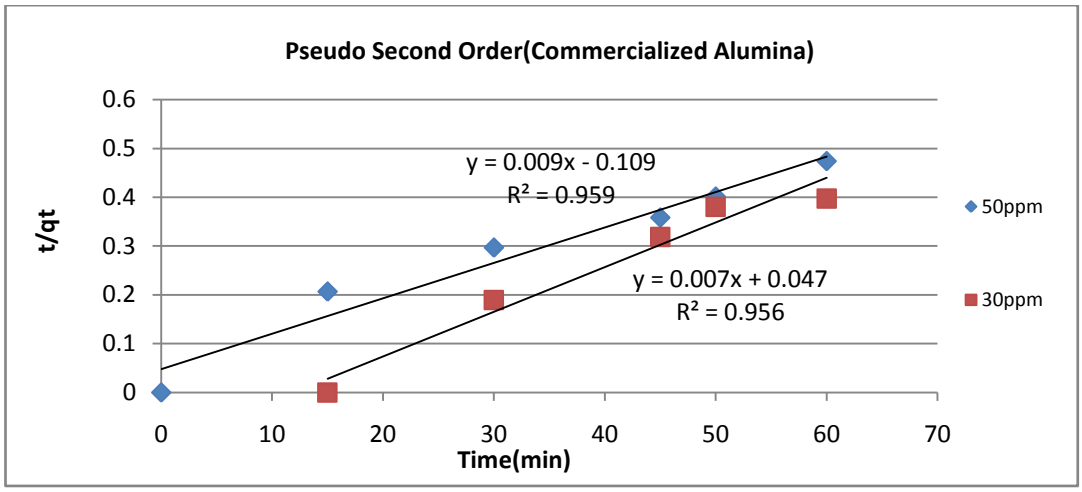

Figure 4.24: Pseudo Second order Reaction for SO_4^{2-} Ions Adsorbed onto Commercialized Alumina at Different Concentrations.

The plots of the pseudo first and second order kinetics graphs should give a straight line if both models are applicable. The constants related to both models are presented in Table 4.3 and Table 4.4.

Table 4.3: Comparison between the Adsorption Rate Constant, q_e Estimated and Correlation Coefficients for Synthesized and Commercialized Alumina for Pseudo First Order

Pseudo First Order	Synthesized Alumina			Commercialized Alumina		
Initial SO_4^{2-} ion Concentration (mg/L)	k_{ad} (min^{-1})	q_e (mg/g)	R^2	k_{ad} (min^{-1})	q_e (mg/g)	R^2
30	0.006909	1.738	0.953	0.006909	7.87	0.896
50	0.006909	3.532	0.764	0.009212	7.907	0.898

Based on comparison made on correlation coefficient value between synthesized and commercialized alumina in Table 3, it can be said that both type of alumina did not follow pseudo first order kinetics. The R^2 value of commercialized alumina is slightly lower than synthesized alumina but shows a good precision for different concentrations tested. Synthesized alumina shows different pattern where increase in

the adsorbate concentration lowers the R^2 value. Further study can be done to study the relation between initial adsorbate concentrations to changes in its kinetic model.

Table 4.4: Comparison between the Adsorption Rate Constant, q_e Estimated and Correlation Coefficients for Synthesized and Commercialized Alumina for Pseudo Second Order

	Synthesized				
Initial SO_4^{2-} ion Concentration.(mg/L	k (g mg $^{-1}$ min^{-1})	q_e (mg/g)	R^2	h (mg g^{-1} min^{-1})	q_e experimental (mg/g)
30	0.0009	76.9231	0.9760	5.2632	80.50
50	0.0012	166.6667	0.9780	34.4828	146.00
	Commercialized				
Initial SO_4^{2-} ion Concentration.(mg/L	k (g mg $^{-1}$ min^{-1})	q_e (mg/g)	R^2	h (mg g^{-1} min^{-1})	q_e experimental (mg/g)
30	0.0010	142.8600	0.9560	21.2800	125.83
50	0.0007	111.1100	0.9590	9.1740	124.50

The plot of t/q_t versus t for pseudo second order model of synthesized alumina yields a very good straight line as compared to commercialized alumina (correlation coefficient,R^2 >0.97).

The theoretical values of q_e for synthesized alumina agree very well with the experimental value. This fact suggests that the adsorption on SO_4^{2-} ions by synthesized alumina follows the pseudo second order kinetic model which relies on the assumption that chemisorptions may be the rate limiting step. The sulphate ion will stick to the alumina surface by forming a chemical bond. Covalent bond was usually formed where adsorbate is tends to find sites that maximize their coordination number with the surface (Sen, T. K. & Sarzali, M. V., 2008).

The analysis on the pseudo graph of synthesized alumina reveals that the value of initial adsorption rate, *h* increases with increase in the initial sulphate concentration. The probability of collisions between metal species is lowered when the concentration of the metal ion in the solution is decreasing. Hence, sulphate ions could be bonded to the active sites on the surface of the adsorbent. The equilibrium adsorption capacity, q_e was increased with increase in initial sulphate concentration.

This shows that higher amount of sulphate ions adsorbed onto alumina surface with increasing amount of sulphate ion in the solution. Large number of sulphate ions is adsorbed at the available adsorption sites (Senthil Kumar and Kirthika, 2009).However, different patterns are observed for commercialized alumina. The value of constants *k,* q_e and *h* are decrease when initial sulphate concentration in the solution is increased. These show that more adsorption occur when less adsorbate ion is presence in the solution.

CHAPTER 5

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The mesoporous alumina with higher surface area and narrow pore size distributions has been synthesized from simple precipitation method. From the results obtained,synthesized alumina has shown better adsorbent characteristics and higher adsorption performance as compared to commercialized alumina.

Result from BET showed that the synthesized alumina particles have mesoporous structure and exhibited narrow pore size distribution. The FTIR studies confirmed the formation of alumina and the adsorption of sulphate ion.The pore structure and adsorption ability have been proved visually using FESEM studies. The surface morphology images show that synthesized alumina formed higher porosity particles as compared to commercialized alumina.

In adsorption contact time experiment, the adsorption rate was rapid over an initial period of time and then decreases gradually until reached constant adsorption after the equilirium point.The adsorption is optimized at the initial concentration of 50 ppm. Both Freundlich and Langmuir models were fitted to the experimental data with relatively good applicability.The kinetic study shows that both aluminas follow pseudo second order kinetics model.

In this project, it was clearly proven that synthesized aluminium oxide was better than commercial aluminium oxide in terms of the morphology and also the capability of adsorbing sulphate ions.

5.2 Recommendations

For further studies, it is recommended also to characterize the alumina using Thermogravimetric Analysis (TGA) and X-ray Diffraction (XRD) to investigate the rate

of change in the weight of alumina as a function of temperature or time and to reveal the chemical structural changes associated with the sorption process respectively.

There are not enough adsorption parameters investigated in adsorption studies.For more information of the adsorption capacity of the alumina, the effect of temperature of solution,amount of adsorbate,and pH towards adsorption of sulphate need to be studied. It is important to find out the optimum parameters for the effective adsorption process in order to manipulate the adsorption process.

Since synthetic sulphate solution is being used in this project, another series of experimental works using aqueous stream that contain sulphate ion is recommended if the selectivity of alumina adsorption is being investigated.

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APPENDICES

Appendix I

Calculation for Adsorption Studies

Calculation for Percentage Uptake

The calculation for percentage uptake is as below:

$$\frac{Initial Concentration - Final Concentration}{Initial Concentration} \times 100\% = \text{Percentage uptake}$$

Let say the initial concentration are 40 ppm and the final concentration are 20 ppm, therefore the percent metal uptake is:

$$\frac{40\ ppm - 20\ ppm}{40\ ppm} \times 100\% = 50\%$$

Calculation for Adsorption Capacity

The calculation for adsorption capacity is as below;

$$\frac{Initial\ Concentration - Final\ Concentration}{Weight\ of\ rice\ husk\ in\ gram} \times volume\ of\ solution\ in\ L$$

Let say the initial concentration is 40 ppm and the final concentration is 20 ppm, volume of solution 0.025 L and the weight of adsorbent used is 0.1 gram, therefore the adsorption capacity is

$$\frac{40\ ppm - 20\ ppm}{0.1g \quad Al2O3} \times 0.025\,L = 5\,mg\ sulfate/g\ Al2O3$$

Preparation of sodium sulfate solution

i. **Stock solution**

MW Na_2SO_4 =142.04 g/mol

MW SO4=96 g/mol

1 gram Na_2SO_4 contain 0.676g of SO4

1g Na in relation to MW of salt = 142.04 / 96 = 1.45g

Hence, weigh out 1.45g Sodium sulfate and dissolve in 1 liter volume to make a 1000 ppm sulfate standard solution.

1. 1.45g Na_2SO_4 is weighted by using electronic balance
2. 1.45g Na_2SO_4 is placed in 1000mL volumetric flask and the flask is filled up with distilled water until the 1000mL level.
3. The solution is stirred with magnetic stirrer at 27ºC ± 2 ºC.

ii. Different concentration

Dilution formula: M1V1=M2V2

M1=Concentration of stock solution

V1=Volume of stock solution

M2=Concentration of desired solution

V1=Volume of desired solution

Using the dilution formula, the volume of stock solution that is needed to make different concentration of sodium sulfate solution will be known.

For example: To prepare 30ppm of 500 ml sulfate solution.

From calculation, the stock solution needed to make 30ppm of 500ml solution is 15ml.

1. 15 ml volume of stock solution is inserted into a clean 500ml volumetric flask.
2. Distilled water is inserted carefully into the volumetric flask containing stock solution until reach the 500ml mark.
3. The solution is shake to ensure well mixing.

Appendix II

Summary Report of BET

Surface Area

Single point surface area at P/Po = 0.248583679:	161.4369 m^2/g
BET Surface Area:	166.0590 m^2/g
Langmuir Surface Area:	244.1813 m^2/g
t-Plot Micropore Area:	11.1659 m^2/g
t-Plot External Surface Area:	154.8931 m^2/g
BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width:	184.517 m^2/g
BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width:	206.9448 m^2/g

Pore Volume

Single point adsorption total pore volume of pores less than 2070.641 Å width at P/Po = 0.990578692:	0.360317 cm^3/g
Single point desorption total pore volume of pores less than 678.071 Å width at P/Po = 0.970617038:	0.358984 cm^3/g
t-Plot micropore volume:	0.003825 cm^3/g
BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width:	0.366289 cm^3/g
BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width:	0.364433 cm^3/g

Pore Size

Adsorption average pore width (4V/A by BET):	86.7926 Å
Desorption average pore width (4V/A by BET):	86.4715 Å
BJH Adsorption average pore width (4V/A):	79.405 Å
BJH Desorption average pore width (4V/A):	70.441 Å

Appendix III

Spreadsheet of Adsorption

Effect of contact time on different initial sulfate concentration for commercialized alumina

Temp:25.7°C pH=6.7 Co 30 ppm

Contact time (min)	Residue Sulfate concentration (ppm),Ct	weight of adsorbent(g), m	Volume of solution(L), V	Initial Sulfate concentration (ppm),Co	mg of sulfate adsorbed/gram of alumina added (mg/g),qt	Percentage sulfate removal (% sulfate removal)
0	30	0.03	0.15	30	0.00	0.00
15	17.5	0.03	0.15	30	62.50	41.67
30	15.7	0.03	0.15	30	71.50	47.67
45	13.9	0.03	0.15	30	80.50	53.67
50	13.4	0.03	0.15	30	83.00	55.33
60	13.2	0.03	0.15	30	84.00	56.00

Temp:25.7°C pH=6.7 Co 50 ppm

Contact time (min)	Residue Sulfate concentration (ppm),Ct	weight of adsorbent(g), m	Volume of solution(L), V	Initial Sulfate concentration (ppm),Co	mg of sulfate adsorbed/gram of alumina added (mg/g),qt	Percentage sulfate removal (% sulfate removal)
0	50	0.03	0.15	50	0.00	0
15	31.5	0.03	0.15	50	92.50	37
30	24	0.03	0.15	50	130.00	52
45	20.8	0.03	0.15	50	146.00	58.4
50	20.4	0.03	0.15	50	148.00	59.2
60	20.8	0.03	0.15	50	146.00	58.4

Temp:25.7°C pH=6.7 Co 10 ppm

Contact time (min)	Residue Sulfate concentration (ppm),Ct	weight of adsorbent(g), m	Volume of solution(L), V	Initial Sulfate concentration (ppm),Co	mg of sulfate adsorbed/gram of alumina added (mg/g),qt	Percentage sulfate removal (% sulfate removal)
0	10	0.03	0.15	10	0.00	0
15	7	0.03	0.15	10	15.00	30
30	6	0.03	0.15	10	20.00	40
45	5.8	0.03	0.15	10	21.00	42
50	5.7	0.03	0.15	10	21.50	43
60	5.3	0.03	0.15	10	23.50	47

Temp:25.7°C pH=6.7 Co 40 ppm

Contact time (min)	Residue Sulfate concentration (ppm),Ct	weight of adsorbent(g),m	Volume of solution(L),V	Initial Sulfate concentration (ppm),Co	mg of sulfate adsorbed/gram of alumina added (mg/g),qt	Percentage sulfate removal (% sulfate removal)
0	40	0.03	0.15	40	0.00	0.00
15	37.9	0.03	0.15	40	10.50	5.25
30	25.9	0.03	0.15	40	70.50	35.25
45	18.6	0.03	0.15	40	129.40	53.50
50	19.7	0.03	0.15	40	101.50	50.75
60	19.1	0.03	0.15	40	104.50	52.25

Temp:25.7°C pH=6.7 Co 20 ppm

Contact time (min)	Residue Sulfate concentration (ppm),Ct	weight of adsorbent(g),m	Volume of solution(L),V	Initial Sulfate concentration (ppm),Co	mg of sulfate adsorbed/gram of alumina added (mg/g),qt	Percentage sulfate removal (% sulfate removal)
0	20	0.03	0.15	20	0.00	0
15	18.2	0.03	0.15	20	9.00	9
30	15.3	0.03	0.15	20	23.50	23.5
45	10.2	0.03	0.15	20	56.40	49
50	10.9	0.03	0.15	20	45.50	45.5

Effect contact time on different initial sulfate concentration for commercialized alumina

Temp:25.7°C pH=6.7 Co 30 ppm

Contact time (min)	Residue Sulfate concentration (ppm),Ct	weight of adsorbent(g),m	Volume of solution(L),V	Initial Sulfate concentration (ppm),Co	mg of sulfate adsorbed/gram of alumina added (mg/g),qt	Percentage sulfate removal (% sulfate removal)
0	30	0.03	0.25	30	0.00	0.00
15	20.5	0.03	0.25	30	79.17	31.67
30	18.7	0.03	0.25	30	94.17	37.67
45	15.8	0.03	0.25	30	118.33	47.33
50	14.9	0.03	0.25	30	125.83	50.33
60	15.6	0.03	0.25	30	120.00	48.00

Temp:25.7°C pH=6.7 Co 50 ppm

Contact time (min)	Residue Sulfate concentration (ppm),Ct	weight of adsorbent(g),m	Volume of solution(L),V	Initial Sulfate concentration (ppm),Co	mg of sulfate adsorbed/gram of alumina added (mg/g),qt	Percentage sulfate removal (% sulfate removal)
0	50	0.03	0.15	50	0.00	0
15	35.5	0.03	0.15	50	72.50	29
30	29.8	0.03	0.15	50	101.00	40.4
45	24.9	0.03	0.15	50	125.50	50.2
50	25.1	0.03	0.15	50	124.50	49.8
60	24.7	0.03	0.15	50	126.50	50.6

Temp:25.7°C pH=6.7 Co 10 ppm

Contact time (min)	Residue Sulfate concentration (ppm),Ct	weight of adsorbent(g),m	Volume of solution(L),V	Initial Sulfate concentration (ppm),Co	mg of sulfate adsorbed/gram of alumina added (mg/g),qt	Percentage sulfate removal (% sulfate removal)
0	10	0.03	0.15	10	0.00	0

15	7.7	0.03	0.15	10	11.50	23
30	7	0.03	0.15	10	15.00	30
45	6.9	0.03	0.15	10	15.50	31
50	6.6	0.03	0.15	10	17.00	34
60	6.5	0.03	0.15	10	17.50	35

Temp:25.7^{o}C pH=6.7 Co 40 ppm

Contact time (min)	Residue Sulfate concentration (ppm),Ct	weight of adsorbent(g), m	Volume of solution(L) ,V	Initial Sulfate concentration (ppm),Co	mg of sulfate adsorbed/ gram of alumina added (mg/g),qt	Percentage sulfate removal (% sulfate removal)
0	40	0.03	0.25	40	0.00	0.00
15	34	0.03	0.25	40	50.00	20.00
30	28	0.03	0.25	40	100.00	40.00
45	24	0.03	0.25	40	133.33	53.33
50	24.6	0.03	0.25	40	128.33	51.33
60	25.9	0.03	0.25	40	117.50	47.00

Temp:25.7^{o}C pH=6.7 Co 20 ppm

Contact time (min)	Residue Sulfate concentration (ppm),Ct	weight of adsorbent(g), m	Volume of solution(L) ,V	Initial Sulfate concentration (ppm),Co	mg of sulfate adsorbed/ gram of alumina added (mg/g),qt	Percentage sulfate removal (% sulfate removal)
0	20	0.03	0.15	20	0.00	0
15	18.4	0.03	0.15	20	8.00	8
30	17.3	0.03	0.15	20	13.50	13.5
45	15.4	0.03	0.15	20	23.00	23
50	15.7	0.03	0.15	20	21.50	21.5
60	16	0.03	0.15	20	20.00	20